SUPPLEMENTARY INFORMATION

Direct α-Alkylation of Primary Aliphatic Amines Enabled by CO_2 and Electrostatics

Juntao Ye,[1] Indrek Kalvet,[2] Franziska Schoenebeck,[2*] Tomislav Rovis[1*]

[1]Department of Chemistry, Columbia University, New York, NY 10027, USA.

[2]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg1, 52074 Aachen, Germany.

[*]Corresponding author:

Email: tr2504@columbia.edu (T.R.); franziska.schoenebeck@rwth-aachen.de (F.S.)

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1. General Information

All solvents were purified by passage through columns of activated alumina or using degassed anhydrous solvents which were purchased from Sigma Aldrich (Sure/Seal bottles) and stored in a glovebox under N_2 atmosphere. CO_2 (99.99%) was purchased from Tech Air. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Thin layer chromatography was conducted on SiliCycle® 250 μm 60 Å (glass-backed). Chromatographic purification was accomplished by flash chromatography on SiliCycle® Silica Flash® 40-63 μm 60 Å or on a Teledyne ISCO Combi*Flash*®*Rf*$^+$ Lumen™ instrument using Redi*Sep*®R_f high performance silica gold column (catalog No. 69-2203-344). The photocatalyst $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**PC1**)[1] and $[Ir(dF(CH_3)ppy)_2(dtbbpy)]PF_6$ (**PC2**)[2] were synthesized according to the reported procedures. Quinuclidine was purchased from Alfa Aesar and stored in a glovebox under N_2. Primary alkyl amines were either commercially available or synthesized according to the reported procedures.[3] All other reagents were purchased from various commercial sources and used as received. Schlenk sealing tubes (25 mL) with high vacuum plug were purchased from Kemtech America Inc. (http://www.kemtech-america.com, catalog No. F580825) and used for the photoredox catalyzed reactions. A Kessil blue LED (34W maximum, 24 VDC, model H150 blue, http://www.kessil.com/horticulture/H150.php) was used as the light source for all the photoredox catalyzed reactions.

^{1}H NMR spectra were recorded on a Bruker AVIII 400 (400 MHz), AVIII 500 (500 MHz) spectrometer and are reported in ppm, relative to tetramethylsilane (TMS, δ 0 ppm) or residual solvent signals ($CDCl_3$ referenced at δ 7.26 ppm, DMSO referenced at δ 2.50 ppm, toluene-d_8 referenced at δ 2.08 ppm). Data are reported as follows: (brs= broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet; coupling constant(s) in Hz; integration). ^{13}C NMR spectra were recorded on a Bruker AVIII 500 (125 MHz) spectrometer and are reported in ppm, relative to residual solvent signals ($CDCl_3$ referenced at δ 77.0 ppm, DMSO referenced at δ 39.52 ppm, toluene-d_8 referenced at δ 20.43 ppm). FT-IR spectra were

recorded on a PerkinElmer Spectrum Two spectrometer. Accurate mass measurements/high resolution mass spectra (HRMS) were obtained from the Columbia University Chemistry Department Mass Spectrometry Facility on a Waters XEVO G2XS QToF mass spectrometer equipped with a UPC2 SFC inlet and a LockSpray source with one of the following three probes: electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, or atmospheric pressure solids analysis probe (ASAP). Elemental analysis was conducted by Midwest Microlab Inc. (http://midwestlab.com/). Stern-Volmer luminescence quenching experiments were conducted on a Fluoromax-4 fluorometer.

2. General Procedure

General Procedure A

To a 25-mL oven-dried Schlenk sealing tube containing a magnetic stir bar were added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (6.6 mg, 0.006 mmol), quinuclidine (11.1 mg, 0.1 mmol), primary alkyl amine (0.3 mmol), acrylate (0.2 mmol), and 0.5 mL of toluene and ^{t}AmOH mixture (1/3, v/v). The reaction tube was sealed, frozen by liquid nitrogen for 10 minutes, and evacuated under vacuum and backfilled with CO_2 (balloon) three times through a three-way stopcock. Liquid nitrogen and the CO_2 balloon were then removed. The reaction tube was sealed and allowed to stand at room temperature for 10 minutes, at which time the plug of the tube was slowly opened to release the excess of CO_2 gas. The tube was then resealed and placed approximately 3 inches away from a Kessil® LED illuminator. The reaction mixture was stirred and irradiated for the indicated period of time. The internal temperature was measured to be approximately 40 ℃ using an infrared thermometer. The crude mixture was then concentrated *in vacuo* and purified by flash chromatography on silica gel with a 4 gram column on a Teledyne ISCO Combi*Flash*® *Rf*$^+$ Lumen™ instrument using the indicated solvent system.

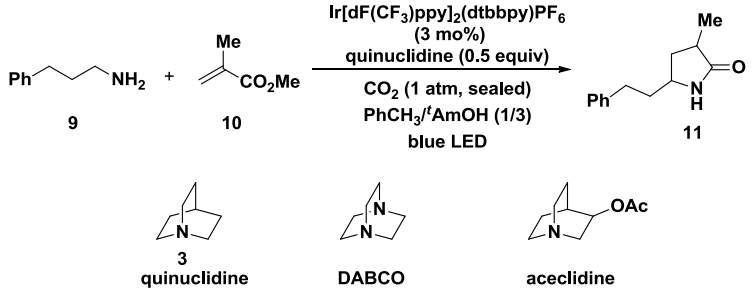
General Procedure B

To a 25-mL oven-dried Schlenk sealing tube containing a magnetic stir bar were added primary alkyl amine (0.6 mmol) and anhydrous toluene (0.5 mL). A CO_2 balloon was then attached to the tube through a three-way stopcock. After stirring for 30 minutes at room temperature, $[Ir(dF(CH_3)ppy)_2(dtbbpy)]PF_6$ (6.0 mg, 0.006 mmol), quinuclidine (11.1 mg, 0.1 mmol), methyl acrylate (18.0 μL, 0.2 mmol, d = 0.956), and anhydrous toluene (0.5 mL) were added sequentially. The reaction tube was sealed, frozen by liquid nitrogen for 10 minutes, and evacuated under vacuum and backfilled with CO_2 (balloon) three times. Liquid nitrogen and the CO_2 balloon were then removed. The reaction tube was sealed and allowed to stand at room temperature

for 10 minutes, at which time the plug of the tube was slowly opened to release the excess of CO_2 gas. The tube was then resealed and placed approximately 3 inches away from a Kessil® LED illuminator. The reaction mixture was stirred and irradiated for the indicated period of time. The internal temperature was measured to be approximately 40 ℃ using an infrared thermometer. The crude mixture was then concentrated *in vacuo* and purified by flash chromatography on silica gel with a 4 gram column on a Teledyne ISCO Combi*Flash*® *Rf*+ Lumen™ instrument using the indicated solvent system.

Supplementary Fig. 1. Photoredox reaction setup. (**A**) Schlenk sealing tube used for the reaction. (**B**) Kessil blue LED used for the reaction. (**C**) Three-way stopcock used for the introduction of CO_2 via a balloon. (**D**) The tube was stirred ~3 inches away from the LED.

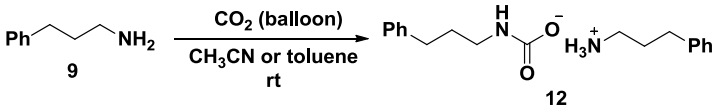
3. Supplementary Table 1 Optimization of reaction conditions[a]



entry	variation from the standard conditions	Yield (%)[b]
1	none	85 (80)
2	K_3PO_4 instead of quinuclidine	<5
3	DABCO instead of quinuclidine	<5
4	aceclidine instead of quinuclidine	72
5	25 mol% of quinuclidine	85
6	10 mol% of quinuclidine	71
7	without [Ir] photocatalyst	0
8	without blue light	0
9	without quinuclidine	<5
10	without CO_2	25[c] (16)

[a] Reactions were conducted on a 0.2 mmol scale according to the General Procedure A. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard, yields in parentheses are isolated yields. [c] *N*-alkylation products and unidentified oligomers were detected by UPLC-MS. ^{t}AmOH, *tert*-amyl alcohol; DABCO, 1,4-diazabicyclo[2.2.2]octane.

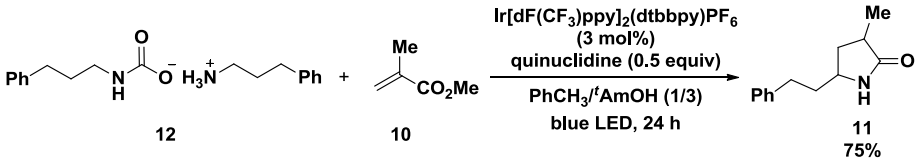
4. Synthesis of Alkylammonium Carbamate 12



Alkylammonium carbamate **12** was prepared according to a reported procedure.[4] To a flame-dried 50-mL Schlenk flask were added 3-phenyl-1-propylamine **9** (0.71 mL, 5 mmol, d = 0.951) and 1 mL of anhydrous CH_3CN or toluene. A CO_2 balloon was then attached to the flask. After stirring at room temperature for 2 hours, a mixture of hexane/ethyl ether (1/1, 50 mL) was added to the flask and the white precipitate was filtered, washed with ethyl ether, dried under vacuum, and stored in a glovebox (0.72 g, 91% yield with CH_3CN; 0.71 g, 90% yield with toluene). **^{1}H NMR** (500 MHz, DMSO): δ = 7.32-7.10 (m, 10 H), 6.56 (brs, 1 H), 6.17 (brs, 3 H), 2.94

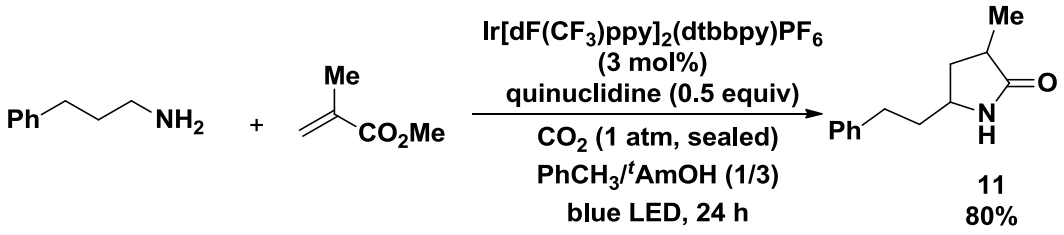
(brs, 2 H), 2.59 (brs, 6 H), 1.69 (brs, 4 H); **^{13}C NMR** (125 MHz, DMSO) δ = 159.8, 142.0, 141.9, 128.3, 128.2, 125.6, 40.1, 33.0, 32.6, 32.4, 31.9; **IR** (CH_2Cl_2, cm^{-1}) 3264, 3061, 3028, 2940, 2867, 2636, 2551, 2230, 1643, 1564, 1493, 1453, 1402, 1355, 1300, 1192, 1162, 1074, 1028; elemental analysis calculated (%) for $C_{19}H_{26}N_2O_2$: C 72.58, H 8.33, N 8.91; found: C 72.38, H 8.14, N 8.68.

Preparation of γ-Lactam 11 from Alkylammonium Carbamate 12 without CO_2

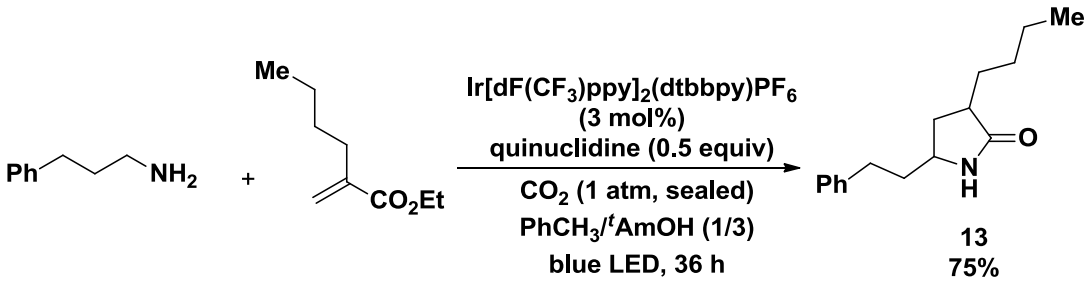


To a 25-mL oven-dried Schlenk sealing tube containing a magnetic stir bar were added photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (6.6 mg, 0.006 mmol), quinuclidine (11.1 mg, 0.1 mmol), alkylammonium carbamate **12** (47.2 mg, 0.15 mmol), methyl methacrylate (20.2 mg, 0.2 mmol), and a mixture of toluene/^{t}AmOH (1/3, v/v, 0.5 mL) in a glovebox. The reaction tube was sealed, taken out of the glovebox, and placed approximately 3 inches away from a Kessil® LED illuminator. The reaction mixture was stirred and irradiated for 24 hours. The internal temperature was measured to be approximately 40 ℃ using an infrared thermometer. The crude reaction mixture was concentrated and purified with 10-20% ethyl acetate in dichloromethane as eluent to give **11** (30.6 mg, 75% yield based on methyl methacrylate) as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33-7.14 (m, 5 H), 6.92 (brs, 0.5 H), 6.79 (brs, 0.5 H), 3.67-3.44 (m, 1 H), 2.72-2.60 (m, 2 H), 2.57-2.39 (m, 1.5 H), 2.06-1.97 (m, 0.5 H), 1.94-1.72 (m, 2.5 H), 1.38-1.27 (m, 0.5 H), 1.22-1.16 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.7, 180.3, 141.0, 140.9, 128.54, 128.53, 128.3, 126.2, 126.1, 52.0, 51.6, 38.5, 38.2, 37.0, 36.6, 35.5, 35.0, 32.40, 32.38, 16.3, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3210, 2968, 2932, 2867, 1689, 1495, 1455, 1265, 1059, 1032; **HRMS** (ASAP) calculated for $C_{13}H_{18}NO$ [$M+H^+$]: 204.1388, found: 204.1389.

5. Synthesis and Characterization of Products

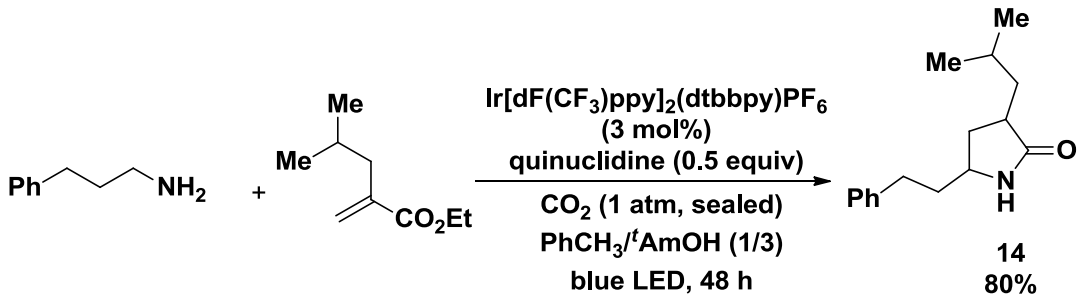


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **11** (32.4 mg, 80%) was obtained as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33-7.14 (m, 5 H), 6.92 (brs, 0.5 H), 6.79 (brs, 0.5 H), 3.67-3.44 (m, 1 H), 2.72-2.60 (m, 2 H), 2.57-2.39 (m, 1.5 H), 2.06-1.97 (m, 0.5 H), 1.94-1.72 (m, 2.5 H), 1.38-1.27 (m, 0.5 H), 1.22-1.16 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.7, 180.3, 141.0, 140.9, 128.54, 128.53, 128.3, 126.2, 126.1, 52.0, 51.6, 38.5, 38.2, 37.0, 36.6, 35.5, 35.0, 32.40, 32.38, 16.3, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3210, 2968, 2932, 2867, 1689, 1495, 1455, 1265, 1059, 1032; **HRMS** (ASAP) calculated for $C_{13}H_{18}NO$ [$M+H^+$]: 204.1388, found: 204.1389.

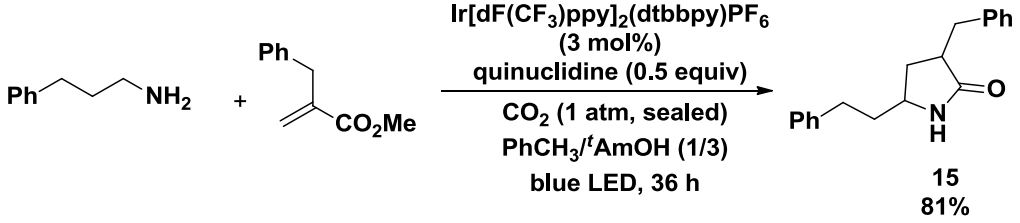


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **13** (36.6 mg, 75%) was obtained as a light yellow oil consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 2 H), 7.23-7.15 (m, 3 H), 6.82 (brs, 0.4 H), 6.70 (brs, 0.6 H), 3.61-3.50 (m, 1 H), 2.73-2.60 (m, 2 H), 2.46-2.30 (m, 1.6 H), 1.98-1.72 (m, 4 H), 1.40-1.26 (m, 5.4 H), 0.96-0.84 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.3, 180.0, 141.1, 141.0, 128.48, 128.47, 128.3, 126.1, 126.0, 52.1, 51.9, 41.8, 40.3, 38.6, 38.4, 34.7, 33.2, 32.34, 32.31, 30.9, 30.8, 29.52, 29.46, 22.6, 14.0; **IR** (CH_2Cl_2, cm^{-1}) 3206, 2929, 2859, 1688, 1455, 1382, 1265, 1062, 1031; **HRMS** (ASAP)

calculated for $C_{16}H_{24}NO$ [M+H$^+$]: 246.1858, found: 246.1857.

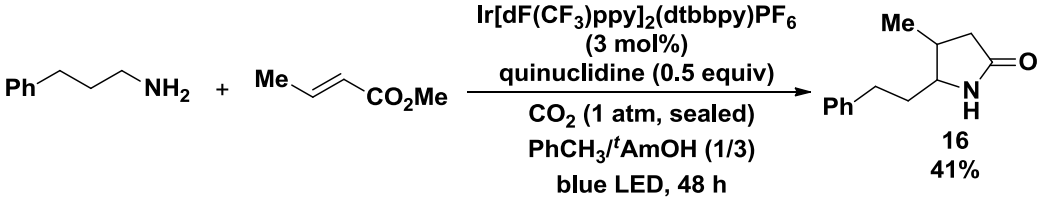


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **14** (39.2 mg, 80%) was obtained as a light yellow solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.32-7.24 (m, 2 H), 7.23-7.15 (m, 3 H), 7.07 (brs, 0.4 H), 6.94 (brs, 0.6 H), 3.62-3.50 (m, 1 H), 2.73-2.60 (m, 2 H), 2.52-2.37 (m, 1.6 H), 2.00-1.60 (m, 4.4 H), 1.35-1.17 (m, 2 H), 0.98-0.85 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.7, 180.4, 141.1, 141.0, 128.4, 128.3, 126.05, 126.01, 52.2, 51.8, 40.4, 40.3, 40.1, 38.53, 38.46, 38.3, 35.3, 33.6, 32.31, 32.26, 26.09, 26.06, 23.5, 23.4, 21.4, 21.3; **IR** (CH_2Cl_2, cm^{-1}) 3205, 3027, 2954, 2925, 2868, 1688, 1496, 1455, 1385, 1305, 1265, 1060, 1032; **HRMS** (ASAP) calculated for $C_{16}H_{24}NO$ [M+H$^+$]: 246.1858, found: 246.1856.

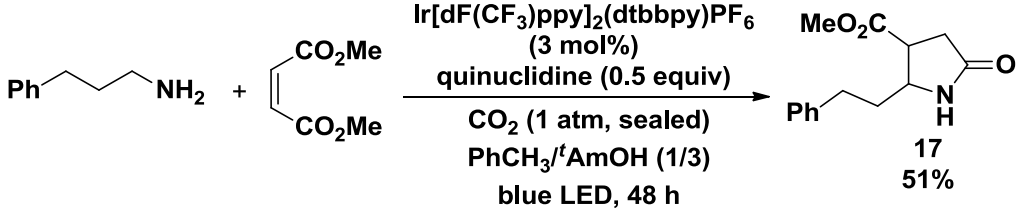


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **15** (45.2 mg, 81%) was obtained as a light yellow oil consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.32-7.11 (m, 10 H), 6.86 (brs, 0.4 H), 6.79 (brs, 0.6 H), 3.55-3.47 (m, 0.6 H), 3.46-3.39 (m, 0.4 H), 3.28 (dd, J_1 = 13.5 Hz, J_2 = 3.5 Hz, 0.6 H), 3.19 (dd, J_1 = 13.8 Hz, J_2 = 3.8 Hz, 0.4 H), 2.81-2.55 (m, 4 H), 2.28-2.19 (m, 0.6 H), 2.04-1.96 (m, 0.4 H), 1.85-1.64 (m, 2.4 H), 1.44-1.35 (m, 0.6 H); **^{13}C NMR** (125

MHz, $CDCl_3$) δ = 179.2, 178.9, 140.9, 139.6, 139.3, 128.95, 128.86, 128.5, 128.4, 128.3, 128.2, 126.3, 126.2, 126.1, 126.0, 52.1, 51.8, 43.6, 42.2, 38.3, 38.2, 36.9, 36.8, 34.0, 32.4, 32.2, 32.1; **IR** (CH_2Cl_2, cm^{-1}) 3210, 3027, 2925, 1688, 1602, 1496, 1454, 1386, 1265, 1064, 1030; **HRMS** (ASAP) calculated for $C_{19}H_{22}NO$ [M+H^+]: 280.1701, found: 280.1702.

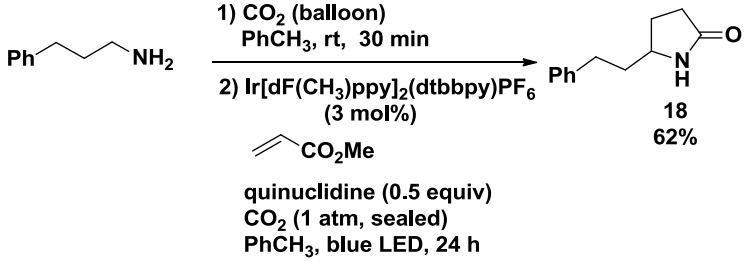


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **16** (16.7 mg, 41%) was obtained as a white solid consisting of two diastereoisomers (2.3:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33-7.27 (m, 2 H), 7.24-7.15 (m, 3 H), 6.38 (brs, 0.3 H), 6.29 (brs, 0.7 H), 3.63-3.56 (m, 0.3 H), 3.22-3.16 (m, 0.7 H), 2.75-2.65 (m, 1.7 H), 2.65-2.55 (m, 0.6 H), 2.55-2.41 (m, 1 H), 2.18-2.08 (m, 0.7 H), 2.04-1.88 (m, 1.7 H), 1.82-1.67 (m, 1.3 H), 1.12 (d, *J* = 7.0 Hz, 2.1 H), 1.04 (d, *J* = 7.0 Hz, 0.9 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.8, 177.4, 141.03, 140.95. 128.60, 128.58, 128.31, 128.26, 126.2, 61.5, 57.0, 38.51, 38.47, 37.1, 35.7, 32.9. 32.8, 32.7, 32.4, 19.1, 14.7; **IR** (CH_2Cl_2, cm^{-1}) 3204, 2925, 2860, 1688, 1495, 1454, 1379, 1267, 1055, 1030; **HRMS** (ASAP) calculated for $C_{13}H_{18}NO$ [M+H^+]: 204.1388, found: 204.1392.

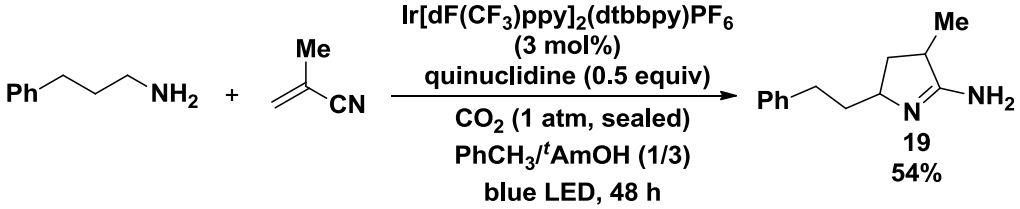


According to the **General Procedure A**, purified with 1% methanol in dichloromethane as eluent, **17** (25.2 mg, 51%) was obtained as a light yellow solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 2 H), 7.23-7.15 (m, 3 H), 7.07 (brs, 0.4 H), 6.85

(brs, 0.6 H), 3.90-3.84 (m, 1.0 H), 3.74 (s, 1.8 H), 3.73 (s, 1.2 H), 3.40-3.47 (m, 0.4 H), 2.97-2.91 (m, 0.6 H), 2.83-2.57 (m, 3.8 H), 2.47-2.40 (m, 0.4 H), 2.07-1.98 (m, 0.6 H), 1.91-1.82 (m, 0.6 H), 1.77-1.71 (m, 0.6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 176.5, 175.7, 173.0, 171.6, 140.6, 140.5, 128.5, 128.33, 128.27, 126.21, 126.18, 56.8, 54.8, 52.4, 52.0, 45.0, 43.4, 38.1, 33.7, 33.6, 32.6, 32.3, 32.2; **IR** (CH_2Cl_2, cm^{-1}) 3203, 3055, 2951, 2857, 1735, 1695, 1496, 1437, 1366, 1265, 1202, 1170, 1030; **HRMS** (ASAP) calculated for $C_{14}H_{18}NO_3$ [M+H$^+$]: 248.1287, found: 248.1288.

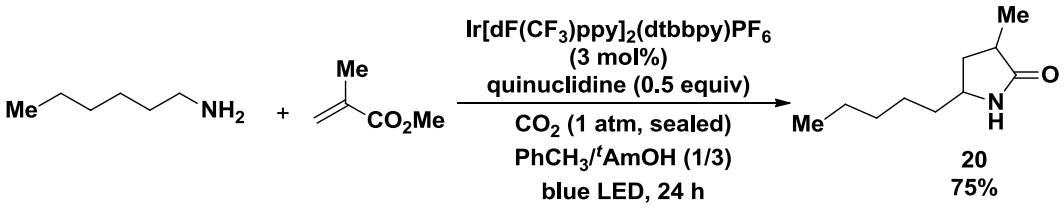


According to the **General Procedure B**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **18** (23.4 mg, 62%) was obtained as a white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.34-7.24 (m, 2 H), 7.24-7.13 (m, 3 H), 6.55 (brs, 1 H), 3.69-3.60 (m, 1 H), 2.67 (t, *J* = 8.0 Hz, 2 H), 2.41-2.20 (m, 3 H), 1.94-1.68 (m, 3 H). Spectral data were consistent with previous report.[5]

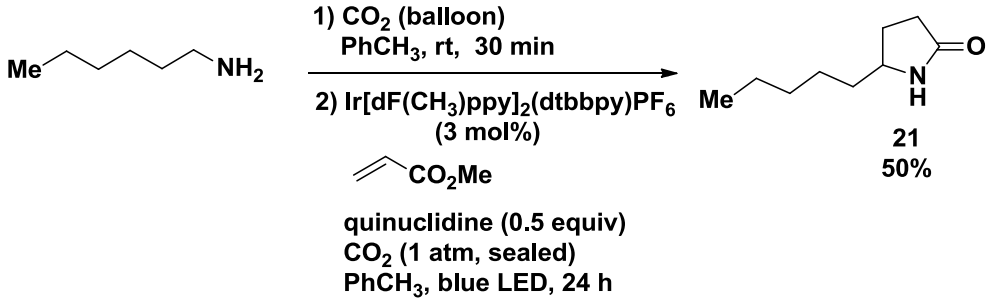


According to the **General Procedure A**, the reaction was carried out with using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (6.6 mg, 0.06 mmol, 3 mol%), quinuclidine (11.1 mg, 0.1 mmol), 3-phenylpropan-1-amine (27.0 mg, 0.2 mmol), and methacrylonitrile (17.4 mg, 0.26 mmol) in 0.5 mL of toluene and ^{t}AmOH mixture (1/3, v/v). After stirring for 48 h under blue LED irradiation, the crude reaction mixture was purified with dichloromethane/MeOH/NH_4OH (6/1/1) as eluent, **19** (21.9 mg, 54%) was obtained as an oil consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31-7.23 (m, 2 H), 7.23-7.13 (m, 3 H), 4.46 (brs, 2

H), 3.82-3.73 (m, 0.4 H), 3.65-3.54 (m, 0.6 H), 2.83-2.60 (m, 3 H), 2.40-2.30 (m, 0.6 H), 1.97-1.63 (m, 2.8 H), 1.24-1.13 (m, 3.6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.7, 170.4, 142.23, 142.18, 128.35, 128.27, 125.68, 125.66, 62.5, 62.2, 39.4, 39.2, 39.1, 38.9, 38.7, 38.1, 33.1, 33.0, 17.7, 17.3; **IR** (CH_2Cl_2, cm^{-1}) 3500-2500 (br), 3174, 3025, 2927, 2857, 1689, 1643, 1602, 1494, 1454, 1375, 1328, 1176, 1030; **HRMS** (ASAP) calculated for $C_{13}H_{19}N_2$ [M+H$^+$]: 203.1548, found: 203.1551.

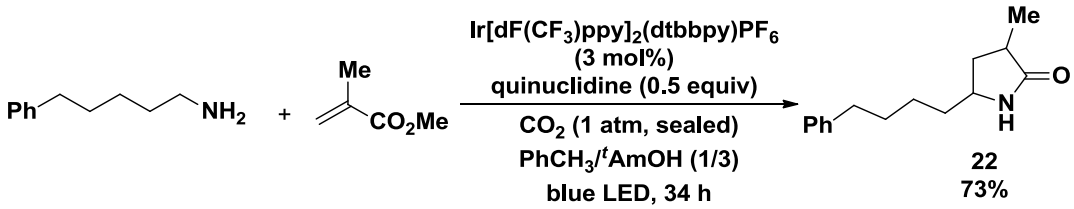


According to the **General Procedure A**, purified with 10-15% ethyl acetate in dichloromethane as eluent, **20** (25.3 mg, 75%) was obtained as a light yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.54 (brs, 0.5 H), 6.45 (brs, 0.5 H), 3.57-3.46 (m, 1 H), 2.52-2.37 (m, 1.5 H), 1.99-1.92 (m, 0.5 H), 1.89-1.81 (m, 0.5 H), 1.58-1.36 (m, 2 H), 1.35-1.21 (m, 6.5 H), 1.20-1.15 (m, 3 H), 0.91-0.83 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.6, 180.2, 52.5, 52.2, 37.1, 36.8, 36.7, 36.5, 35.5, 35.0, 31.6, 25.6, 25.5, 22.49, 22.47, 16.3, 16.0, 13.9; **IR** (CH_2Cl_2, cm^{-1}) 3206, 2957, 2926, 2858, 1694, 1456, 1373, 1296, 1252, 1058, 1033; **HRMS** (ASAP) calculated for $C_{10}H_{20}NO$ [M+H$^+$]: 170.1545, found: 170.1546.

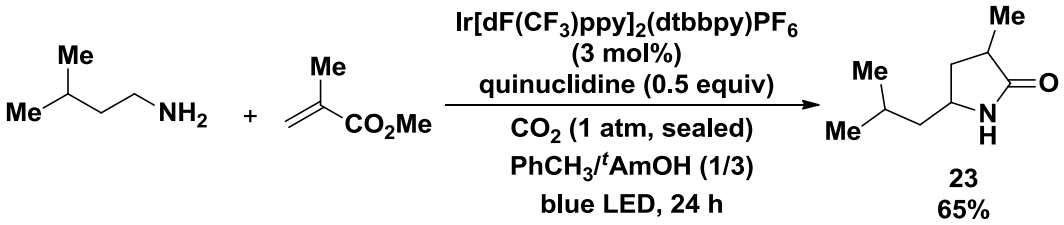


According to the **General Procedure B**, purified with 10-15% ethyl acetate in dichloromethane as eluent, **21** (15.5 mg, 50%) was obtained as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.29 (brs, 1 H), 3.65-3.58 (m, 1 H), 2.38-2.19 (m, 3 H), 1.74-1.65

(m, 1 H), 1.56-1.42 (m, 2 H), 1.35-1.26 (m, 6 H), 0.88 (t, *J* = 6.8 Hz, 3 H). Spectral data were consistent with previous report.[6]

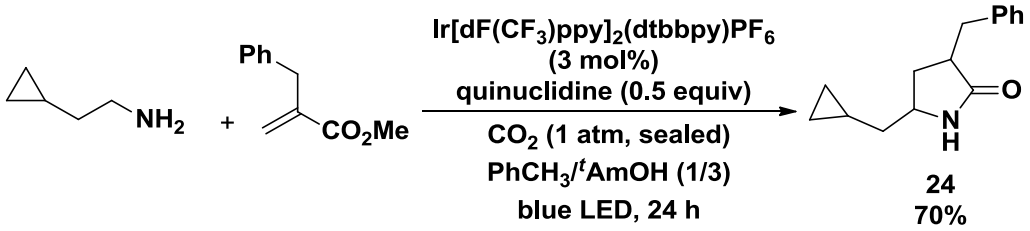


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **22** (33.8 mg, 73%) was obtained as a light yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34-7.25 (m, 2 H), 7.24-7.15 (m, 3 H), 6.82 (brs, 0.5 H), 6.73 (brs, 0.5 H), 4.61-3.48 (m, 1 H), 2.69-2.59 (m, 2 H), 2.56-2.37 (m, 1.5 H), 2.02-1.93 (m, 0.5 H), 1.92-1.82 (m, 0.5 H), 1.72-1.23 (m, 6.5 H), 1.23-1.17 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.8, 180.4, 142.19, 142.17, 128.25, 128.21, 125.6, 52.5, 52.1, 36.9, 36.7, 36.6, 36.3, 35.68, 35.65, 35.4, 35.1, 31.2, 25.5, 25.4, 16.2, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3205, 3025, 2928, 2857, 1690, 1495, 1454, 1296, 1258, 1069, 1030; **HRMS** (ESI) calculated for $C_{15}H_{22}NO$ [M+H$^+$]: 232.1701, found: 232.1703.

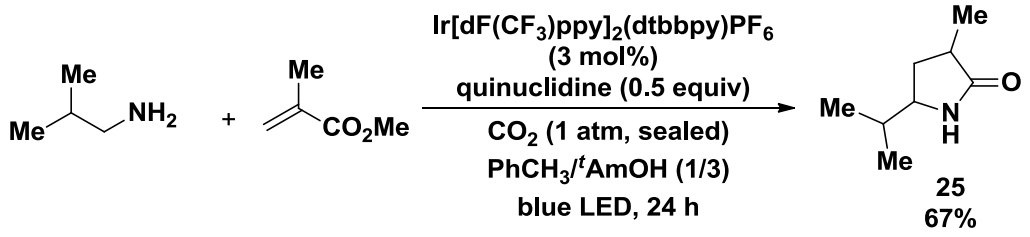


According to the **General Procedure A**, purified with 10-15% ethyl acetate in dichloromethane as eluent, **23** (20.2 mg, 65%) was obtained as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.35 (brs, 0.5 H), 6.24 (brs, 0.5 H), 3.67-3.56 (m, 1 H), 2.52-2.38 (m, 1.5 H), 1.97-1.83 (m, 1 H), 1.68-1.56 (m, 1 H), 1.48-1.38 (m, 1 H), 1.34-1.23 (m, 1.5 H), 1.20-1.16 (m, 3 H), 0.94-0.88 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.6, 180.2, 50.6, 50.2, 46.1, 45.6, 37.6, 36.6, 35.9, 34.9, 25.4, 25.3, 22.9, 22.8, 22.6, 22.3, 16.3, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3215, 2959, 2930, 2871, 1690, 1457,

1386, 1368, 1298, 1265, 1059; **HRMS** (ASAP) calculated for $C_9H_{18}NO$ [M+H$^+$]: 156.1388, found: 156.1390.

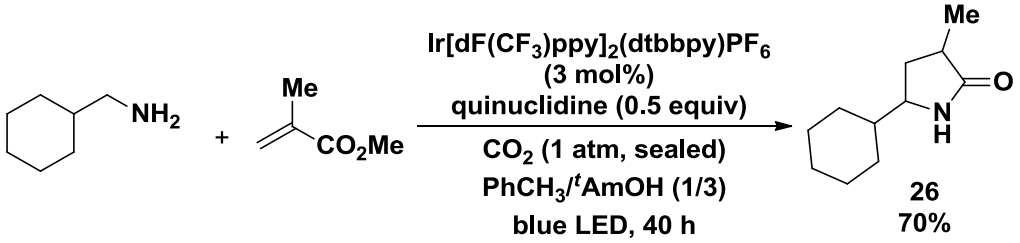


According to the **General Procedure A**, purified with 10-15% ethyl acetate in dichloromethane as eluent, **24** (32.1 mg, 70%) was obtained as a light yellow solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33-7.25 (m, 2 H), 7.25-7.17 (m, 3 H), 6.48 and 6.43 (brs, 1 H), 3.65-3.51 (m, 1 H), 3.28 (dd, J_1 = 13.8 Hz, J_2 = 3.8 Hz, 0.6 H), 3.20 (dd, J_1 = 13.5 Hz, J_2 = 4.0 Hz, 0.4 H), 2.80-2.58 (m, 2 H), 2.29-2.22 (m, 0.6 H), 2.05-1.97 (m, 0.4 H), 1.86-1.79 (m, 0.4 H), 1.50-1.36 (m, 1.6 H), 1.28-1.21 (m, 0.4 H), 1.18-1.11 (m, 0.6 H), 0.67-0.57 (m, 1 H), 0.51-0.40 (m, 2 H), 0.11-0.00 (m, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.0, 178.6, 139.6, 139.4, 129.0, 128.9, 128.4, 126.3, 126.2, 53.1, 52.8, 43.6, 42.1, 41.4, 41.3, 36.8, 34.1, 32.3, 7.7, 7.6, 4.51, 4.49, 3.8, 3.7; **IR** (CH_2Cl_2, cm^{-1}) 3211, 3082, 3024, 2918, 1685, 1495, 1453, 1426, 1385, 1306, 1100, 1017; **HRMS** (ASAP) calculated for $C_{15}H_{20}NO$ [M+H$^+$]: 230.1545, found: 230.1540.

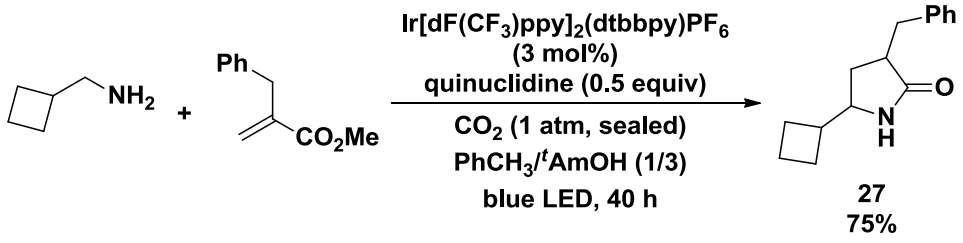


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **25** (19.0 mg, 67%) was obtained as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.57 (brs, 0.5 H), 6.47 (brs, 0.5 H), 3.34-3.28 (m, 0.5 H), 3.27-3.20 (m, 0.5 H), 2.50-2.40 (m, 1 H), 2.37-2.30 (m, 0.5 H), 2.07-2.00 (m, 0.5 H), 1.83-1.75 (m, 0.5 H), 1.67-1.51 (m, 1 H), 1.34-1.26 (m, 0.5 H), 1.18 (d, J = 7.5 Hz, 3

H), 0.96-0.85 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 181.0, 180.5, 58.6, 58.1, 36.7, 35.5, 34.5, 33.5, 33.3, 33.0, 19.3, 18.6, 18.2, 17.9, 16.7, 15.9; **IR** (CH_2Cl_2, cm^{-1}) 3212, 2960, 2831, 2873, 1684, 1454, 1389, 1370, 1291, 1271, 1119, 1067; **HRMS** (ASAP) calculated for $C_8H_{16}NO$ [M+H$^+$]: 142.1232, found: 142.1234.

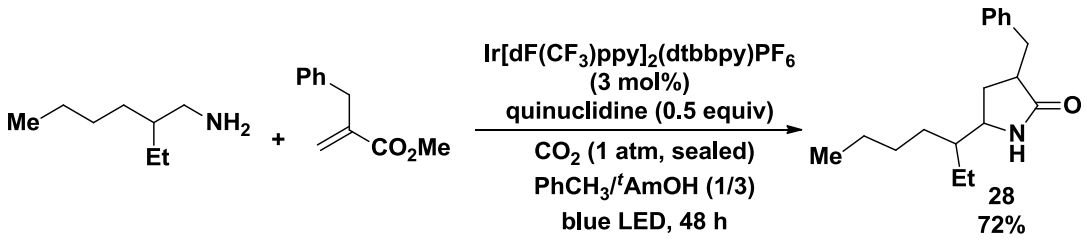


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **26** (25.5 mg, 70%) was obtained as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.36 (brs, 0.5 H), 6.23 (brs, 0.5 H), 3.35-3.20 (m, 1 H), 2.48-2.30 (m, 1.5 H), 2.10-2.03 (m, 0.5 H), 1.82-1.63 (m, 5.5 H), 1.37-1.07 (m, 7.5 H), 1.01-0.84 (m, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.8, 180.3, 57.5, 57.1, 43.4, 43.1, 36.5, 35.3, 34.8, 33.1, 29.9, 29.1, 28.8, 28.4, 26.3, 25.9, 25.8, 25.73, 25.71, 16.6, 15.9; **IR** (CH_2Cl_2, cm^{-1}) 3206, 3084, 2923, 2849, 1681, 1454, 1392, 1292, 1274, 1249, 1115, 1051, 1033; **HRMS** (ASAP) calculated for $C_{11}H_{20}NO$ [M+H$^+$]: 182.1545, found: 182.1547.

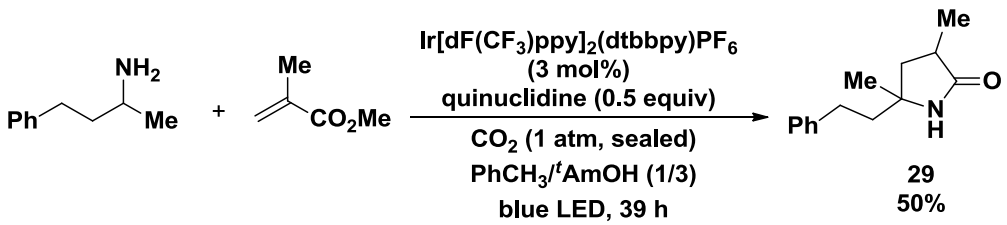


According to the **General Procedure A**, purified with 10-15% ethyl acetate in dichloromethane as eluent, **27** (34.5 mg, 75%) was obtained as a light yellow solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.32-7.25 (m, 2 H), 7.25-7.16 (m, 3 H), 6.45 (brs, 0.4 H), 6.32 (brs, 0.4 H), 3.56-3.47 (m, 0.6 H), 3.44-3.37 (m, 0.4 H), 3.27 (dd, J_1 = 13.8 Hz, J_2 = 3.8 Hz, 0.6 H), 3.20 (dd, J_1 = 13.5 Hz, J_2 = 3.5 Hz, 0.4 H), 2.77-2.67 (m, 1 H), 2.67-2.56 (m,

1 H), 2.34-2.08 (m, 1.6 H), 2.03-1.57 (m, 6.4 H), 1.31-1.22 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.2, 178.9, 139.6, 139.4, 129.0, 128.9, 128.42, 128.40, 126.3, 126.2, 56.6, 56.5, 43.7, 42.2, 40.33, 40.28, 37.0, 36.8, 31.3, 30.2, 24.23, 24.19, 24.1, 23.9, 17.9, 17.8; **IR** (CH_2Cl_2, cm^{-1}) 3209, 3053, 2973, 2932, 2862, 1688, 1496, 1454, 1386, 1336, 1264, 1030; **HRMS** (ASAP) calculated for $C_{15}H_{20}NO$ [M+H$^+$]: 230.1545, found: 230.1549.

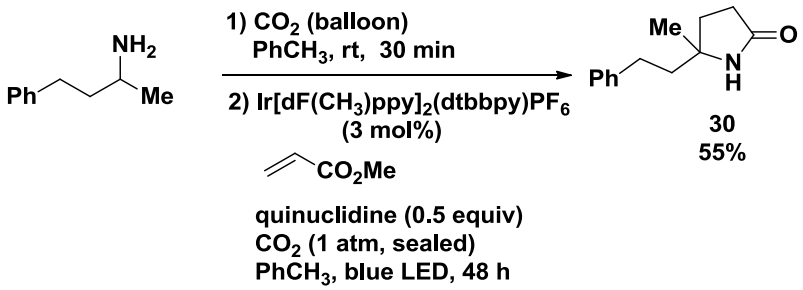


According to the **General Procedure A**, purified with 5-10% ethyl acetate in dichloromethane as eluent, **28** (39.3 mg, 72%) was obtained as an oil consisting of four diastereoisomers (1.5:1.5:1:1 ratio as determined by ^{1}H and ^{13}C NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33-7.18 (m, 5 H), 6.36 (brs, 0.4 H), 6.29 (brs, 0.6 H), 3.53-3.46 (m, 0.6 H), 3.45-3.38 (m, 0.4 H), 3.28 (dt, J_1 = 13.5 Hz, J_2 = 3.3 Hz, 0.6 H), 3.18 (dd, J_1 = 13.5 Hz, J_2 = 3.5 Hz, 0.4 H), 2.77-2.58 (m, 2 H), 2.15-2.07 (m, 0.6 H), 1.95-1.80 (m, 1 H), 1.46-1.05 (m, 9.4 H), 0.93-0.80 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.3, 178.7, 139.68, 139.66, 139.4, 128.99, 128.98, 128.89, 128.87, 128.4, 126.3, 126.2, 54.9, 54.7, 54.6, 54.4, 44.2, 44.0, 43.8, 43.58, 43.56, 42.5, 37.2, 36.69, 36.67, 31.5, 31.4, 29.65, 29.60, 29.13, 29.11, 29.0, 28.9, 28.8, 28.6, 28.3, 28.0, 23.03, 23.01, 22.99, 22.4, 22.2, 21.8, 21.6, 14.0, 11.2, 11.0, 10.7, 10.5; **IR** (CH_2Cl_2, cm^{-1}) 3202, 3085, 2957, 2926, 2870, 1691, 1495, 1454, 1380, 1265, 1058, 1032; **HRMS** (ASAP) calculated for $C_{18}H_{28}NO$ [M+H$^+$]: 274.2171, found: 274.2177.

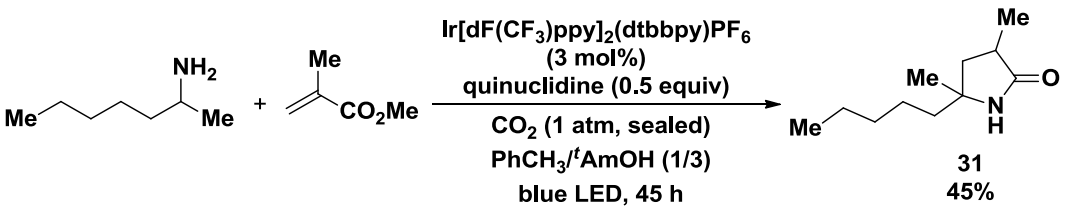


According to the **General Procedure A**, purified with 10-20% ethyl acetate in

dichloromethane as eluent, **29** (21.7 mg, 50%) was obtained as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35-7.26 (m, 2 H), 7.25-7.15 (m, 3 H), 6.34 (brs, 0.5 H), 6.25 (brs, 0.5 H), 2.74-2.57 (m, 3 H), 2.37-2.30 (m, 0.5 H), 2.20-2.13 (m, 0.5 H), 1.92-1.74 (m, 2 H), 1.70-1.54 (m, 1 H), 1.37 and 1.33 (s, 3 H), 1.27-1.21 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.4, 179.2, 141.50, 141.45, 128.50, 128.47, 128.23, 128.17, 126.02, 125.97, 56.78, 56.76, 44.5, 43.9, 42.8, 42.4, 36.2, 35.6, 30.9, 30.7, 28.3, 26.6, 16.7, 16.1; **IR** (CH_2Cl_2, cm^{-1}) 3205, 3026, 2963, 2929, 2869, 1689, 1496, 1454, 1381, 1240, 1113, 1064, 1032; **HRMS** (ASAP) calculated for $C_{14}H_{20}NO$ [M+H$^+$]: 218.1545, found: 218.1541.

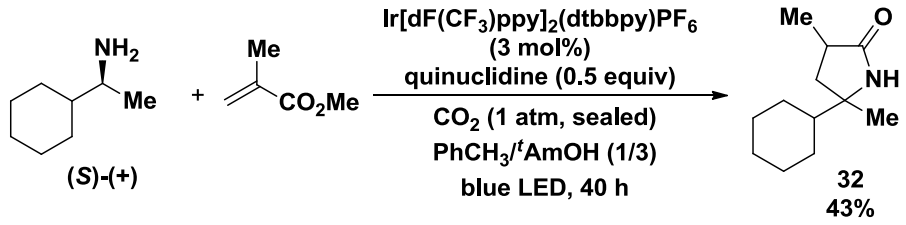


According to the **General Procedure B**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **30** (22.3 mg, 55%) was obtained as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.31-7.25 (m, 2 H), 7.21-7.15 (m, 3 H), 6.65 (brs, 1 H), 2.71-2.58 (m, 2 H), 2.45-2.39 (m, 2 H), 2.07-2.00 (m, 1 H), 1.95-1.78 (m, 3 H), 1.33 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 177.3, 141.5, 128.5, 128.2, 126.0, 59.1, 44.0, 33.5, 30.7, 30.4, 27.2; **IR** (CH_2Cl_2, cm^{-1}) 3202, 3052, 2926, 2851, 1687, 1496, 1454, 1421, 1381, 1265, 1239, 1070, 1031; **HRMS** (ASAP) calculated for $C_{13}H_{18}NO$ [M+H$^+$]: 204.1388, found: 204.1390.

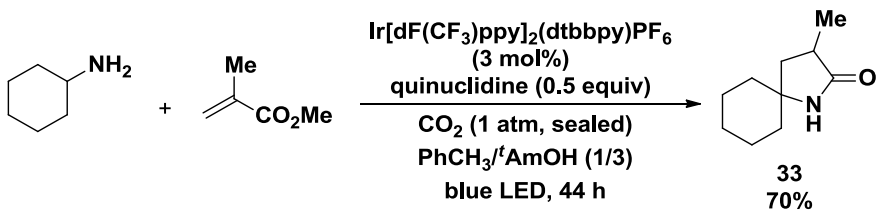


According to the **General Procedure A**, purified with 10-15% ethyl acetate in

dichloromethane as eluent, **31** (16.4 mg, 45%) was obtained as a light yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.74 and 5.71 (brs, 1 H), 2.66-2.50 (m, 1 H), 2.28-2.20 (m, 0.5 H), 2.12-2.04 (m, 0.5 H), 1.60-1.43 (m, 3 H), 1.37-1.22 (m, 8 H), 1.22-1.17 (m, 4 H), 0.93-0.84 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.3, 179.0, 56.7, 42.8, 42.5, 41.9, 36.2, 35.6, 32.14, 32.11, 28.3, 26.5, 24.1, 23.9, 22.55, 22.52, 16.6, 16.1, 14.0; **IR** (CH_2Cl_2, cm^{-1}) 3214, 2959, 2929, 2860, 1691, 1456, 1422, 1379, 1310, 1245, 1182, 1057, 1033; **HRMS** (ASAP) calculated for $C_{11}H_{22}NO$ [M+H^{+}]: 184.1701, found: 184.1697.

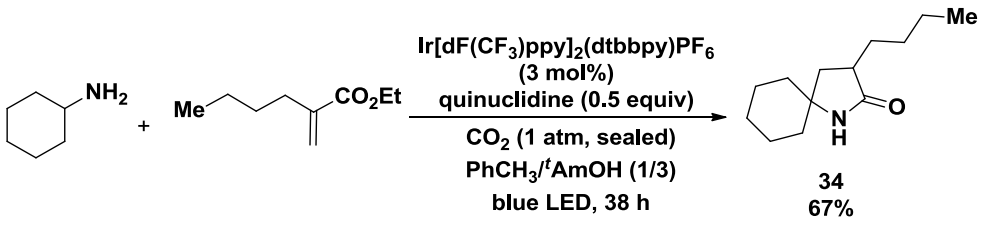


According to the **General Procedure A**, purified with 10-15% ethyl acetate in dichloromethane as eluent, **32** (16.7 mg, 43%) was obtained as a light yellow solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.18 and 6.14 (brs, 1 H), 2.62-2.45 (m, 1 H), 2.40-2.32 (m, 0.5 H), 2.04-1.97 (m, 0.5 H), 1.82-1.58 (m, 5 H), 1.57-1.50 (m, 0.5 H), 1.40-1.33 (m, 0.5 H), 1.33-0.85 (m, 12 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.4, 179.1, 59.5, 59.3, 48.6, 47.5, 41.4, 40.7, 36.3, 35.3, 27.8, 27.6, 27.3, 27.2, 26.5, 26.4, 26.34, 26.31, 26.1, 22.9, 17.1, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3206, 2926, 2853, 1687, 1449, 1380, 1303, 1267, 1033; **HRMS** (ASAP) calculated for $C_{12}H_{22}NO$ [M+H^{+}]: 196.1701, found: 196.1707.

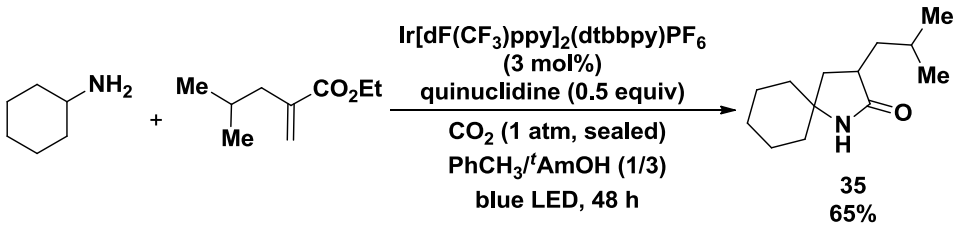


According to the **General Procedure A**, purified with 10-20% ethyl acetate in

dichloromethane as eluent, **33** (23.3 mg, 70%) was obtained as a white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.20 (brs, 1 H), 2.61-2.50 (m, 1 H), 2.24 (dd, J_1 = 12.6 Hz, J_2 = 9.0 Hz, 1 H), 1.62-1.34 (m, 11 H), 1.19 (d, J = 7.2 Hz, 3 H). Spectral data were consistent with previous report.[7]

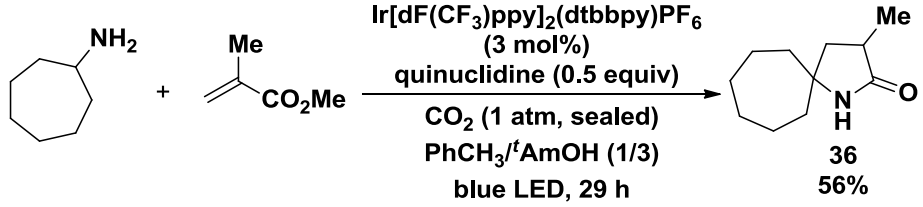


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **34** (27.9 mg, 67%) was obtained as a white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.42 (brs, 1 H), 2.50-2.40 (m, 1 H), 2.17 (dd, J_1 = 12.5 Hz, J_2 = 9.0 Hz, 1 H), 1.95-1.82 (m, 1 H), 1.58-1.22 (m, 16 H), 0.89 (t, J = 6.8 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 178.8, 57.0, 40.6, 39.6, 39.4, 37.8, 31.2, 29.5, 25.1, 23.1, 23.0, 22.6, 14.0; **IR** (CH_2Cl_2, cm^{-1}) 3179, 3072, 2921, 2854, 1683, 1449, 1432, 1377, 1339, 1277, 1256, 1180, 1141, 1001; **HRMS** (ASAP) calculated for $C_{13}H_{24}NO$ [M+H$^+$]: 210.1858, found: 210.1855.

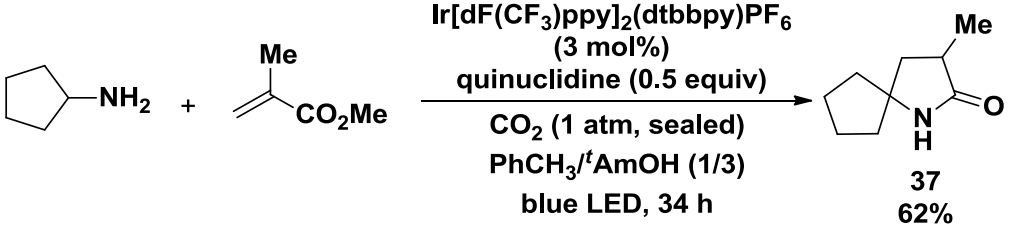


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **35** (27.3 mg, 65%) was obtained as a light yellow solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.33 (brs, 1 H), 2.55-2.46 (m, 1 H), 2.19 (dd, J_1 = 12.5 Hz, J_2 = 9.0 Hz, 1 H), 1.81-1.72 (m, 1 H), 1.70-1.59 (m, 1 H), 1.58-1.46 (m, 8 H), 1.45-1.34 (m, 3 H), 1.26-1.16 (m, 1 H), 0.92 (d, J = 6.5 Hz, 3 H), 0.88 (d, J = 6.5 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.1, 57.0, 40.9, 40.0, 39.7, 38.7, 37.7, 26.1, 25.1, 23.5, 23.09, 23.05, 21.3; **IR** (CH_2Cl_2, cm^{-1}) 3195, 2929, 2857, 1684, 1452, 1385, 1341, 1264, 1178, 1001; **HRMS** (ASAP) calculated for $C_{13}H_{24}NO$ [M+H$^+$]: 210.1858,

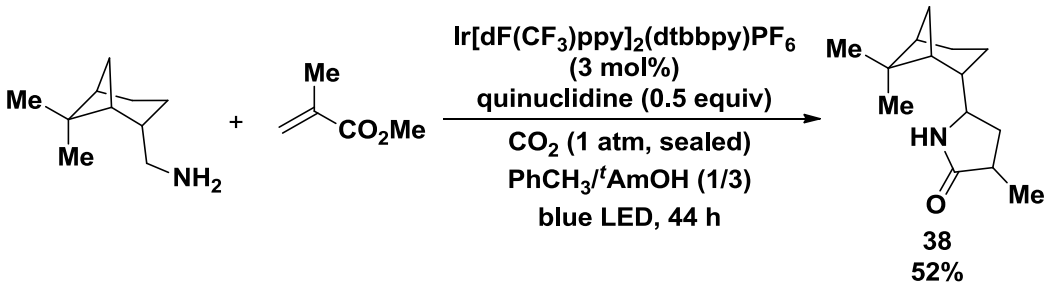
found: 210.1865.



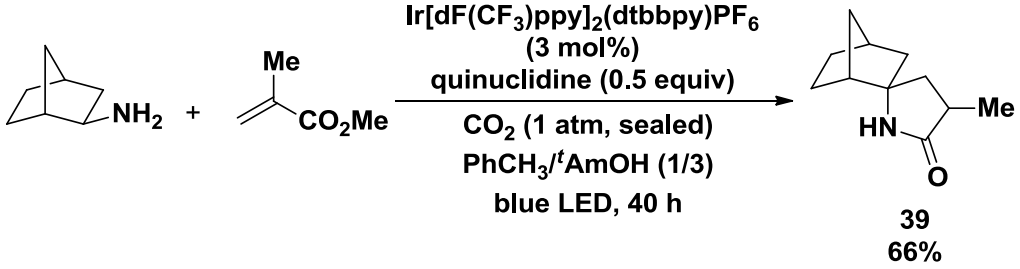
According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **36** (20.2 mg, 56%) was obtained as a white solid: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.18 (brs, 1 H), 2.60-2.48 (m, 1 H), 2.23 (dd, J_1 = 12.6 Hz, J_2 = 8.6 Hz, 1 H), 1.81-1.34 (m, 13 H), 1.18 (d, J = 7.2 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.0, 60.0, 43.6, 43.0, 40.2, 35.2, 28.8, 28.7, 22.7, 22.6, 16.1; **IR** (CH_2Cl_2, cm^{-1}) 3176, 3077, 2924, 2851, 1684, 1454, 1379, 1346, 1262, 1207, 1069, 1049; **HRMS** (ASAP) calculated for $C_{11}H_{20}NO$ [M+H$^+$]: 182.1545, found: 182.1539.



According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **37** (19.0 mg, 62%) was obtained as a white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.30 (brs, 1 H), 2.60-2.51 (m, 1 H), 2.24 (dd, J_1 = 12.3 Hz, J_2 = 8.8 Hz, 1 H), 1.79-1.60 (m, 9 H), 1.19 (d, J = 7.5 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.4, 64.6, 42.8, 39.8, 38.9, 36.3, 23.4, 23.0, 16.1; **IR** (CH_2Cl_2, cm^{-1}) 3206, 2960, 2873, 1687, 1454, 1379, 1265, 1099, 1033; **HRMS** (ASAP) calculated for $C_9H_{16}NO$ [M+H$^+$]: 154.1232, found: 154.1227.

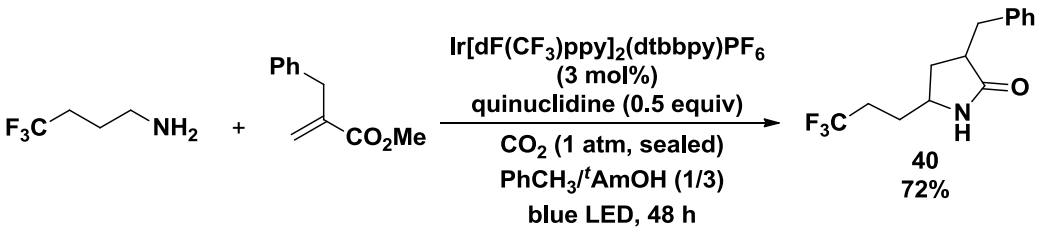


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **38** (23.1 mg, 52%) was obtained as a white solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.12 (brs, 0.5 H), 6.02 (brs, 0.5 H), 3.58-3.51 (m, 1 H), 2.49-2.33 (m, 2.5 H), 2.01-1.80 (m, 7 H), 1.45-1.35 (m, 1 H), 1.25-1.21 (m, 0.5 H), 1.21-1.15 (m, 6 H), 1.01-0.98 (m, 3 H), 0.88 (dd, J_1 = 10 Hz, J_2 = 5 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.5, 180.2, 56.3, 56.1, 48.6, 46.6, 43.5, 42.9, 41.1, 41.0, 38.6, 36.6, 34.4, 34.3, 32.9, 32.7, 28.0, 27.9, 25.9, 25.8, 23.4, 23.3, 18.6, 17.7, 16.2, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3211, 2935, 2869, 1690, 1456, 1384, 1264, 1058, 1033; **HRMS** (ASAP) calculated for $C_{14}H_{24}NO$ [M+H$^+$]: 222.1858, found: 222.1854.

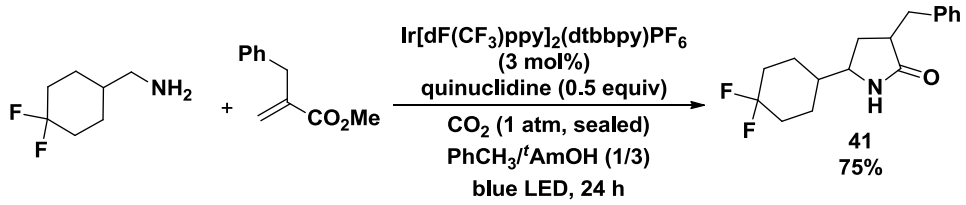


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **39** (23.5 mg, 66%) was obtained as a white solid consisting of two diastereoisomers (2.3:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.34 (brs, 1 H), 2.58-2.44 (m, 1 H), 2.36-2.11 (m, 2 H), 2.09-2.06 (m, 0.3 H), 2.03-1.99 (m, 0.7 H), 1.82-1.76 (m, 0.7 H), 1.76-1.70 (m, 0.7 H), 1.69-1.40 (m, 4.6 H), 1.34-1.21 (m, 3 H), 1.21-1.13 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.1, 179.8, 63.4, 62.8, 48.7, 46.78, 46.76, 46.7, 46.4, 45.7, 37.9, 37.4, 36.9, 36.4, 36.3, 36.1, 28.6, 28.3, 23.5, 23.1, 16.6, 15.6; **IR** (CH_2Cl_2, cm^{-1}) 3196, 3075, 2955, 2872, 1683, 1454, 1431, 1378, 1366, 1308, 1266, 1245, 1227, 1186, 1112, 1077,

1013; **HRMS** (ASAP) calculated for $C_{11}H_{18}NO$ [M+H$^+$]: 180.1388, found: 180.1384.

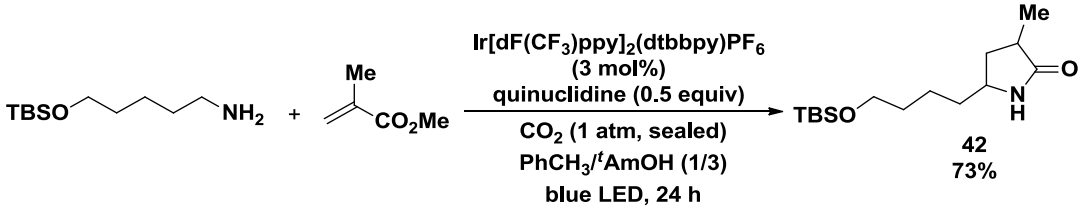


According to the **General Procedure A**, 10-15% ethyl acetate in dichloromethane as eluent, **40** (38.8 mg, 72%) was obtained as a white solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.41-7.16 (m, 6 H), 3.62-3.54 (m, 0.6 H), 3.52-3.44 (m, 0.4 H), 3.27-3.15 (m, 1 H), 2.82-2.72 (m, 1 H), 2.70-2.62 (m, 1 H), 2.30-2.22 (m, 0.6 H), 2.18-2.00 (m, 2.4 H), 1.82-1.58 (m, 2.4 H), 1.42-1.33 (m, 0.6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ^{19}F decoupled) δ = 179.5, 179.2, 139.1, 139.0, 128.94, 128.91, 128.5, 126.7, 126.5, 126.4, 51.4, 51.2, 43.6, 42.0, 36.7, 36.6, 33.1, 32.1, 30.4, 30.1, 28.9, 28.8; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -66.1, -66.2; **IR** (CH_2Cl_2, cm^{-1}) 3208, 3055, 2929, 2860, 1695, 1496, 1454, 1393, 1361, 1264, 1143, 1096, 1063; **HRMS** (ASAP) calculated for $C_{14}H_{17}NOF_3$ [M+H$^+$]: 272.1262, found: 272.1268.

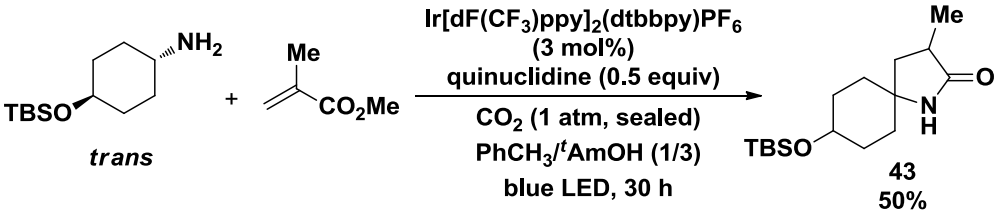


According to the **General Procedure A**, 10-15% ethyl acetate in dichloromethane as eluent, **41** (44.1 mg, 75%) was obtained as a light yellow solid consisting of two diastereoisomers (1.2:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.34-7.17 (m, 5 H), 6.91 (brs, 0.45 H), 6.86 (brs, 0.55 H), 3.33-3.15 (m, 2 H), 2.79-2.60 (m, 2 H), 2.23-2.03 (m, 2.55 H), 2.00-1.93 (m, 0.45 H), 1.91-1.83 (m, 0.45 H), 1.81-1.56 (m, 4 H), 1.46-1.38 (m, 0.55 H), 1.38-1.12 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ^{19}F decoupled) δ = 179.3, 179.0, 139.3, 139.2, 129.0, 128.51, 128.50, 126.4, 126.3, 123.1, 56.5, 56.2, 43.5, 42.3, 41.39, 41.37, 37.0, 36.6, 33.1, 33.0, 31.7, 30.2, 25.8, 25.3, 24.7, 24.4; **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -91.7

(d, J_{FF} = 235.5 Hz), -91.8 (d, J_{FF} = 235.5 Hz), -102.7 (d, J_{FF} = 235.9 Hz), -102.8 (d, J_{FF} = 235.5 Hz); **IR** (CH_2Cl_2, cm^{-1}) 3211, 2941, 2871, 1685, 1496, 1453, 1364, 1265, 1117, 1087; **HRMS** (ASAP) calculated for $C_{17}H_{22}NOF_2$ [M+H^+]: 294.1669, found: 294.1670.

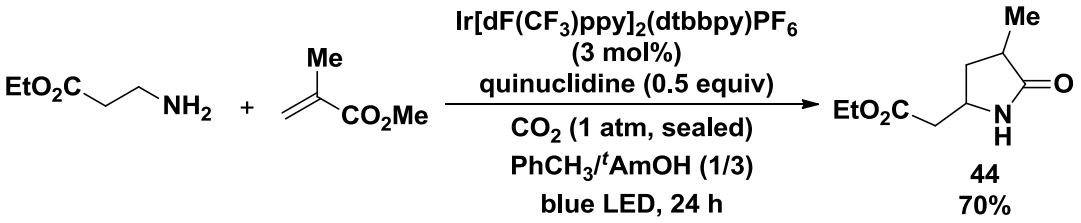


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **42** (41.9 mg, 73%) was obtained as a light yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.41 (brs, 0.5 H), 6.32 (brs, 0.5 H), 3.62-3.48 (m, 3 H), 2.52-2.38 (m, 1.5 H), 2.00-1.93 (m, 0.5 H), 1.90-1.83 (m, 0.5 H), 1.61-1.28 (m, 6 H), 1.29-1.23 (m, 0.5 H), 1.20-1.15 (m, 3 H), 0.88 (s, 9 H), 0.03 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.6, 180.2, 62.79, 62.76, 52.5, 52.1, 37.0, 36.7, 36.6, 36.3, 35.4, 35.0, 32.54, 32.53, 25.9, 22.3, 22.2, 18.3, 16.3, 16.0, -5.3; **IR** (CH_2Cl_2, cm^{-1}) 3209, 2929, 2857, 1695, 1460, 1388, 1360, 1253, 1098, 1033, 1006; **HRMS** (ASAP) calculated for $C_{15}H_{32}NO_2Si$ [M+H^+]: 286.2202, found: 286.2208.

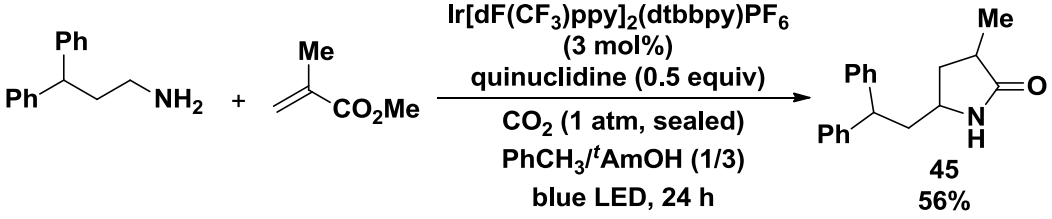


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **43** (30.0 mg, 50%) was obtained as an oil consisting of two diastereoisomers (1.2:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.61 (brs, 0.4 H), 6.09 (brs, 0.5 H), 3.78-3.68 (m, 1 H), 2.61-2.50 (m, 1 H), 2.33-2.17 (m, 1 H), 1.82-1.63 (m, 4 H), 1.56-1.39 (m, 5 H), 1.21-1.17 (m, 3 H), 0.87 (s, 9 H), 0.03 (s, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.5, 179.0, 68.2, 67.8,

56.6, 56.0, 41.4, 36.0, 35.7, 35.4, 35.3, 33.9, 33.8, 31.7, 31.6, 31.5, 25.8, 18.11, 18.10, 16.5, 16.4, -4.78, -4.82; **IR** (CH_2Cl_2, cm^{-1}) 3204, 2930, 2856, 1690, 1454, 1380, 1251, 1102, 1052; **HRMS** (ASAP) calculated for $C_{16}H_{31}NO_2Si$ [M-H^+]: 296.2046, found: 296.2044.

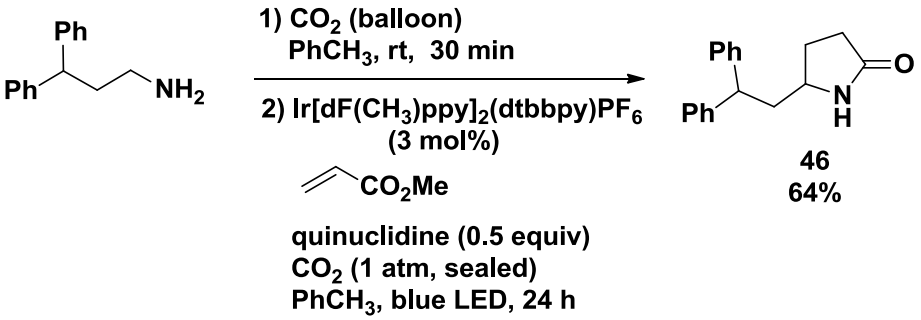


According to the **General Procedure A**, purified with 1-1.5% methanol in dichloromethane as eluent, **44** (25.9 mg, 70%) was obtained as a light yellow solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.23 (brs, 1 H), 4.18-4.11 (m, 2 H), 3.98-3.92 (m, 0.4 H), 3.92-3.84 (m, 0.6 H), 2.58 (dd, J_1 = 16.5 Hz, J_2 = 4.0 Hz, 0.6 H), 2.55-2.37 (m, 3 H), 2.03-1.91 (m, 1 H), 1.33-1.30 (m, 0.4 H), 1.28-1.23 (m, 3 H), 1.21-1.17 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 179.9, 179.7, 171.32, 171.26, 60.93, 60.88, 48.5, 48.2, 41.3, 40.8, 36.4, 36.1, 35.0, 34.5, 16.1, 15.9, 14.1; **IR** (CH_2Cl_2, cm^{-1}) 3227, 2968, 2931, 2874, 1729, 1695, 1456, 1373, 1293, 1249, 1194, 1096, 1029; **HRMS** (ASAP) calculated for $C_9H_{16}NO_3$ [M+H^+]: 186.1130, found: 186.1129.

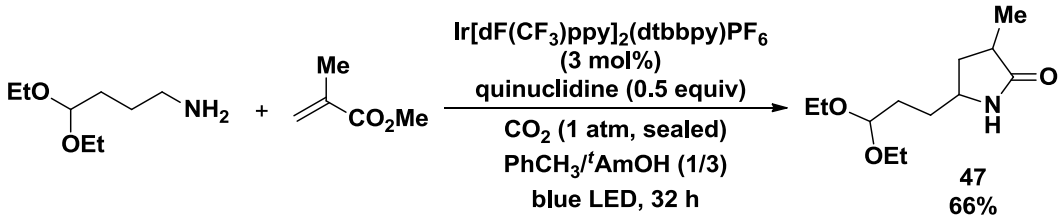


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **45** (31.2 mg, 56%) was obtained as a colorless oil consisting of two diastereoisomers (1.2:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28-7.09 (m, 10 H), 6.32 (brs, 0.45 H), 6.23 (brs, 0.55 H), 3.95 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1 H), 3.45-3.31 (m, 1 H), 2.50-2.39 (m, 0.45 H), 2.39-2.10 (m, 3 H), 2.02-1.92 (m, 0.45 H), 1.72-1.84 (m, 0.55 H), 1.34-1.24 (m, 0.55

H), 1.16-1.07 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.5, 180.1, 144.0, 143.8, 143.7, 143.5, 128.74, 128.68, 128.6, 127.74, 127.66, 127.61, 127.59, 126.7, 126.55, 126.50, 51.0, 50.4, 48.6, 48.4, 42.9, 42.4, 37.3, 36.4, 35.8, 34.8, 16.2, 15.9; **IR** (CH_2Cl_2, cm^{-1}) 3200, 3026, 2965, 2930, 2871, 1689, 1494, 1453, 1294, 1265, 1063, 1032; **HRMS** (ASAP) calculated for $C_{19}H_{22}NO$ [M+H$^+$]: 280.1701, found: 280.1702.

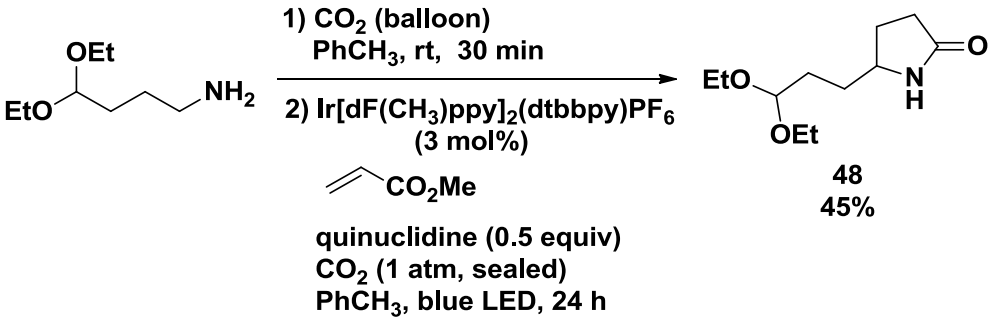


According to the **General Procedure B**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **46** (33.9 mg, 64%) was obtained as a white solid: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.33-7.16 (m, 10 H), 6.45 (brs, 1 H), 4.01 (t, *J* = 8.0 Hz, 1 H), 3.56-3.48 (m, 1 H), 2.38-2.17 (m, 5 H), 1.81-1.71 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 178.1, 143.8, 143.7, 128.71, 128.65, 127.7, 127.6, 126.6, 126.5, 52.9, 48.4, 42.6, 30.0, 27.7; **IR** (CH_2Cl_2, cm^{-1}) 3198, 3056, 2932, 1685, 1495, 1448, 1423, 1395, 1265, 1067, 1031; **HRMS** (ASAP) calculated for $C_{18}H_{20}NO$ [M+H$^+$]: 266.1545, found: 266.1548.

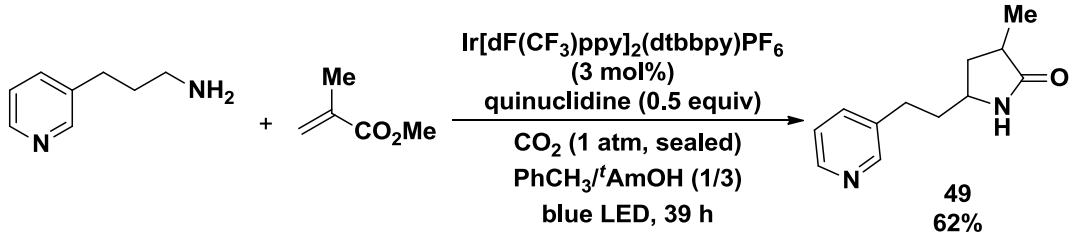


According to the **General Procedure A**, , purified with 10-40% ethyl acetate in dichloromethane as eluent, **47** (30.3 mg, 66%) was obtained as a light yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.41 (brs, 0.5 H), 6.37 (brs, 0.5 H), 4.47-4.44 (m, 1 H), 3.67-3.42 (m, 5 H), 2.52-2.37 (m, 1.5 H), 1.99-1.93 (m, 0.5 H), 1.90-1.83 (m, 0.5 H), 1.67-1.47 (m, 4 H), 1.29-1.25 (m, 0.5 H), 1.22-1.14 (m, 9 H); **^{13}C NMR** (125 MHz,

$CDCl_3$) δ = 180.5, 180.1, 102.53, 102.47, 61.5, 61.4, 61.3, 61.2, 52.3, 51.8, 37.0, 36.7, 35.5, 34.9, 31.7, 31.5, 30.2, 30.1, 16.2, 15.9, 15.3; **IR** (CH_2Cl_2, cm^{-1}) 3214, 2973, 2930, 2873, 1693, 1455, 1373, 1347, 1266, 1123, 1059; **HRMS** (ASAP) calculated for $C_{12}H_{22}NO_3$ [M-H^+]: 228.1600, found: 228.1595.

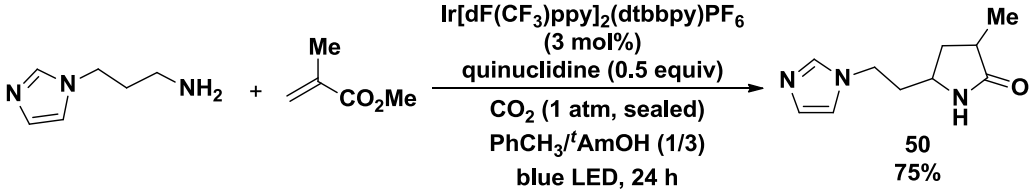


According to the **General Procedure B**, purified with 10-30% ethyl acetate in dichloromethane as eluent, **48** (19.2 mg, 45%) was obtained as an oil: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.25 (brs, 1 H), 4.47 (t, *J* = 5.3 Hz, 1 H), 3.68-3.59 (m, 3 H), 3.52-3.43 (m, 2 H), 2.38-2.19 (m, 3 H), 1.75-1.51 (m, 5 H), 1.23-1.16 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 178.0, 102.5, 61.5, 61.3, 54.2, 31.6, 30.1, 27.3, 15.3; **IR** (CH_2Cl_2, cm^{-1}) 3218, 2975, 2933, 2877, 1689, 1446, 1374, 1346, 1266, 1123, 1057, 1007; **HRMS** (ASAP) calculated for $C_{11}H_{20}NO_3$ [M-H^+]: 214.1443, found: 214.1448.



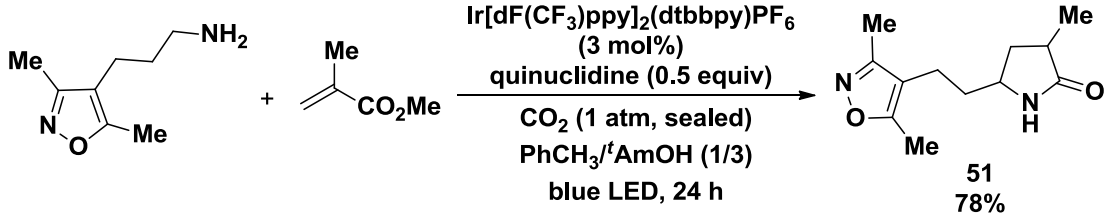
According to the **General Procedure A**, purified with 5-10% methanol in dichloromethane as eluent, **49** (25.2 mg, 62%) was obtained as a white solid consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.47-8.42 (m, 2 H), 7.52-7.48 (m, 1 H), 7.25-7.11 (m, 2 H), 3.64-3.51 (m, 1 H), 2.74-2.59 (m, 2 H), 2.56-2.40 (m, 1.6 H), 2.06-1.97 (m, 0.4 H), 1.95-1.71 (m, 2.4 H), 1.37-1.27 (m, 0.6 H), 1.22-1.16 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 181.0, 180.6, 149.8, 147.6, 136.4, 135.7, 123.4, 51.9, 51.6, 38.2, 38.0, 36.8, 36.7, 35.3, 35.1, 29.4, 29.3, 16.3, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3220, 2929, 2869,

1683, 1576, 1480, 1455, 1424, 1299, 1258, 1029; **HRMS** (ASAP) calculated for $C_{12}H_{17}N_2O$ [M+H$^+$]: 205.1341, found: 205.1346.



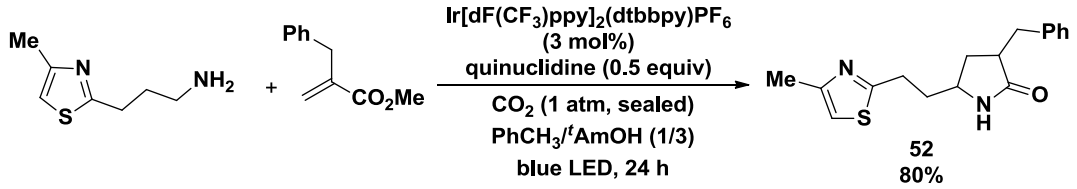
According to the **General Procedure A**, purified with 4-6% methanol in dichloromethane as eluent, **50** (28.9 mg, 75%) was obtained as a light yellow solid consisting of two diastereoisomers (1.2:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.85 (brs, 0.45 H), 7.81 (brs, 0.55 H), 7.61-7.56 (m, 1 H), 7.08 (s, 1 H), 6.98-6.95 (m, 1 H), 4.16-4.05 (m, 2 H), 3.53-3.40 (m, 1 H), 2.57-2.37 (m, 1.55 H), 2.06-1.86 (m, 2.90 H), 1.35-1.27 (m, 0.55 H), 1.23-1.17 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 181.5, 181.2, 137.3, 129.60, 129.59, 118.70, 118.65, 49.6, 49.2, 43.71, 43.68, 38.2, 37.9, 36.7, 36.5, 35.14, 35.11, 16.2, 15.9; **IR** (CH_2Cl_2, cm^{-1}) 3212, 3109, 2966, 2931, 2873, 1687, 1509, 1455, 1288, 1229, 1108, 1080, 1032; **HRMS** (ASAP) calculated for $C_{10}H_{16}N_3O$ [M+H$^+$]: 194.1293, found: 194.1293.

3 mmol scale reaction: According to the **General Procedure A**, the reaction was carried out using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (33.7 mg, 0.03 mmol, 1 mol%), quinuclidine (166.8 mg, 1.5 mmol), 3-(1*H*-imidazol-1-yl)propan-1-amine (563.3 mg, 4.5 mmol), and methyl methacrylate (300.4 mg, 3 mmol) in 6 mL of toluene and ^{t}AmOH mixture (1/3, v/v). After stirring for 40 h under blue LED irradiation, the crude reaction mixture was purified with 4-6% methanol in dichloromethane as eluent to afford **50** (401.4 mg, 69% yield) as a light yellow solid.



According to the **General Procedure A**, purified with 2-3% methanol in dichloromethane as eluent, **51** (34.6 mg, 78%) was obtained as a white solid

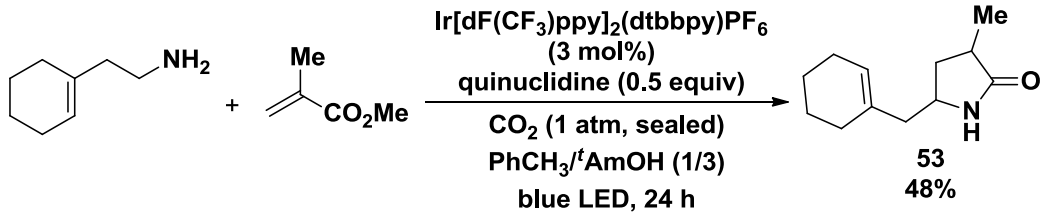
consisting of two diastereoisomers (1.2:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.27 (brs, 0.55 H), 7.23 (brs, 0.45 H), 3.63-3.51 (m, 1 H), 2.57-2.28 (m, 6.55 H), 2.22 and 2.21 (s, 3 H), 2.04-1.97 (m, 0.45 H), 1.96-1.89 (m, 0.45 H), 1.72-1.56 (m, 2 H), 1.36-1.27 (m, 0.55 H), 1.23-1.18 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 181.1, 180.7, 164.73, 164.68, 159.34, 159.32, 112.6, 52.1, 51.8, 36.83, 36.76, 36.6, 35.3, 35.2, 18.8, 16.3, 15.9, 10.8, 10.2; **IR** (CH_2Cl_2, cm^{-1}) 3217, 2966, 2930, 2869, 1689, 1638, 1454, 1424, 1265, 1195, 1035; **HRMS** (ASAP) calculated for $C_{12}H_{19}N_2O_2$ [M+H$^+$]: 223.1447, found: 223.1447.



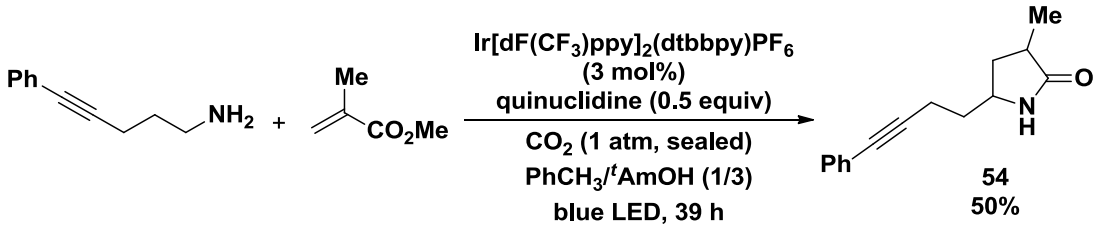
According to the **General Procedure A**, purified with 1-3% methanol in dichloromethane as eluent, **52** (48.0 mg, 80%) was obtained as a yellow oil consisting of two diastereoisomers (1.5:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.25-7.31 (m, 2 H), 7.24-7.17 (m, 3 H), 6.83 and 6.81 (brs, 1 H), 6.73-6.70 (m, 1 H), 3.63-3.55 (m, 0.6 H), 3.52-3.45 (m, 0.4 H), 3.27 (dd, J_1 = 13.5 Hz, J_2 = 4.0 Hz, 0.6 H), 3.19 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 0.4 H), 3.03-2.91 (m, 2 H), 2.81-2.59 (m, 2 H), 2.42-2.38 (m, 3 H), 2.29-2.21 (m, 0.6 H), 2.06-1.99 (m, 0.4 H), 1.98-1.79 (m, 2.4 H), 1.46-1.39 (m, 0.6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 178.9, 178.6, 168.7, 168.6, 152.4, 139.5, 139.2, 128.94, 128.86, 128.4, 126.3, 126.2, 112.64, 112.62, 51.9, 51.5, 43.6, 42.0, 36.80, 36.75, 36.42, 36.39, 33.8, 32.3, 29.8, 29.7, 17.0; **IR** (CH_2Cl_2, cm^{-1}) 3217, 3026, 2921, 2858, 1688, 1530, 1495, 1441, 1303, 1269, 1078, 1030; **HRMS** (ASAP) calculated for $C_{17}H_{21}N_2OS$ [M+H$^+$]: 301.1375, found: 301.1369.

1 mmol scale reaction: According to the **General Procedure A**, the reaction was carried out using [Ir(dF(CF_3)ppy)$_2$(dtbbpy)]PF_6 (22.4 mg, 0.02 mmol, 2 mol%), quinuclidine (55.6 mg, 0.5 mmol), 3-(4-methylthiazol-2-yl)propan-1-amine (234.1 mg, 1.5 mmol), and methyl 2-benzylacrylate (176.2 mg, 1 mmol) in 2.5 mL of toluene and ^{t}AmOH mixture (1/3, v/v). After stirring for 40 h under blue LED irradiation, the

crude reaction mixture was purified with 1-3% methanol in dichloromethane as eluent to afford **52** (225.8 mg, 75% yield) as a yellow oil.

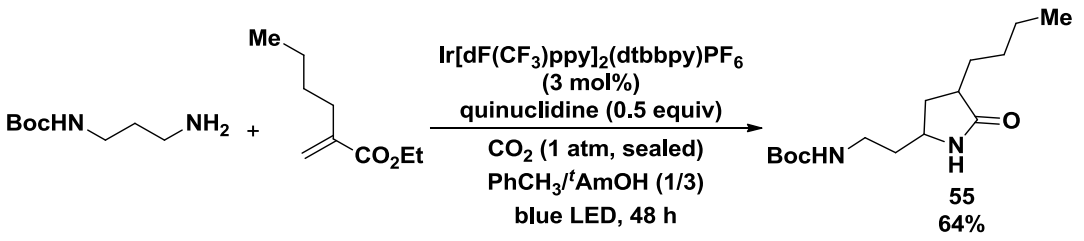


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **53** (18.6 mg, 48%) was obtained as a light yellow solid consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 5.75 and 5.72 (brs, 1 H), 5.48 and 5.46 (s, 1 H), 3.74-3.62 (m, 1 H), 2.53-2.36 (m, 1.5 H), 2.18-1.81 (m, 7 H), 1.65-1.48 (m, 4 H), 1.34-1.26 (m, 0.5 H), 1.21-1.17 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.2, 180.0, 134.1, 133.9, 124.6, 124.5, 50.0, 49.8, 45.7, 45.2, 37.2, 36.9, 35.3, 35.1, 28.4, 28.3, 25.2, 22.79, 22.77, 22.3, 16.3, 15.9; **IR** (CH_2Cl_2, cm^{-1}) 3213, 2924, 2833, 1694, 1455, 1436, 1301, 1265, 1033, 1058; **HRMS** (ASAP) calculated for $C_{12}H_{20}NO$ [M+H$^+$]: 194.1545, found: 194.1541.

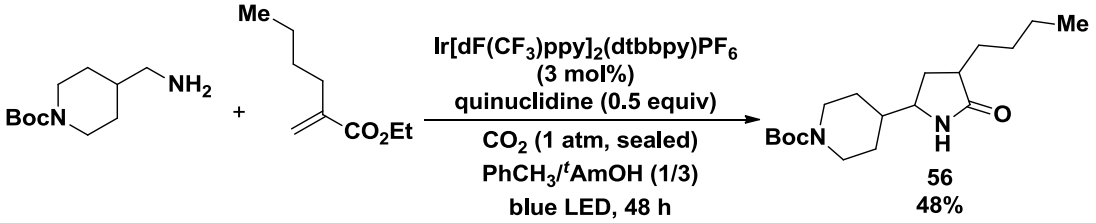


According to the **General Procedure A**, purified with 10-20% ethyl acetate in dichloromethane as eluent, **54** (22.9 mg, 50%) was obtained as a yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.44-7.38 (m, 2 H), 7.31-7.24 (m, 3 H), 6.38 (brs, 1 H), 3.83-3.70 (m, 1 H), 2.55-2.43 (m, 3.5 H), 2.10-2.02 (m, 0.5 H), 2.00-1.91 (m, 0.5 H), 1.87-1.72 (m, 2 H), 1.40-1.34 (m, 0.5 H), 1.24-1.19 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.5, 180.1, 131.5, 128.2, 127.9, 127.8, 123.34, 123.30, 88.32, 88.28, 81.7, 81.6, 51.9, 51.3, 36.9, 36.4, 35.4, 35.0, 34.8, 16.5, 16.4, 16.2, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3213, 2968,

2928, 2870, 1690, 1490, 1456, 1441, 1264, 1070, 1032; **HRMS** (ASAP) calculated for $C_{15}H_{18}NO$ [M+H$^+$]: 228.1388, found: 228.1383.

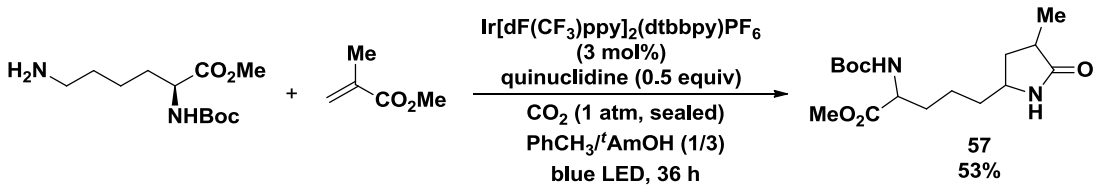


According to the **General Procedure A**, purified with 20-30% ethyl acetate in dichloromethane as eluent, **55** (36.5 mg, 64%) was obtained as a light yellow solid consisting of two diastereoisomers (1.2:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.99 (brs, 0.45 H), 6.91 (brs, 0.55 H), 4.82 (brs, 1 H), 3.53-3.63 (m, 1 H), 3.30-3.07 (m, 2 H), 2.44-2.30 (m, 1.55 H), 1.99-1.75 (m, 2 H), 1.74-1.52 (m, 2 H), 1.41 (s, 9 H), 1.35-1.25 (m, 5.45 H), 0.88 (t, *J* = 6.5 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.1, 180.0, 156.3, 156.2, 79.4, 50.3, 49.7, 41.8, 40.1, 37.5, 37.4, 37.1, 34.5, 33.3, 30.82, 30.77, 29.5, 29.4, 28.3, 22.58, 22.56, 13.9; **IR** (CH_2Cl_2, cm^{-1}) 3348, 3202, 2963, 2930, 2859, 1682, 1524, 1454, 1390, 1365, 1277, 1251, 1167, 1043; **HRMS** (ASAP) calculated for $C_{15}H_{27}N_2O_3$ [M-H$^+$]: 283.2022, found: 283.2025.



According to the **General Procedure A**, purified with 10-30% ethyl acetate in dichloromethane as eluent, **56** (31.2 mg, 48%) was obtained as a light yellow oil consisting of two diastereoisomers (1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.29 and 6.24 (brs, 1 H), 4.17 (brs, 2 H), 3.39-3.25 (m, 1 H), 2.66 (brs, 2 H), 2.42-2.30 (m, 1.5 H), 2.07-1.99 (m, 0.5 H), 1.96-1.77 (m, 1.5 H), 1.71-1.60 (m, 2.5 H), 1.46 (s, 9 H), 1.40-1.27 (m, 6 H), 1.24-1.06 (m, 2 H), 0.95-0.88 (m, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 180.4, 180.1, 154.7, 79.5, 57.1, 56.8, 41.8,

41.7, 40.5, 32.2, 31.1, 30.7, 29.49, 29.46, 28.4, 27.8, 27.5, 22.59, 22.57, 13.9; **IR** (CH_2Cl_2, cm^{-1}) 3209, 2958, 2929, 2857, 1685, 1422, 1365, 1278, 1252, 1229, 1165, 1091, 1011; **HRMS** (ASAP) calculated for $C_{18}H_{31}N_2O_3$ [M-H^+]: 323.2335, found: 323.2336.



According to the **General Procedure A**, purified with 1-3% methanol in dichloromethane as eluent, **57** (35.0 mg, 53%) was obtained as an oil consisting of four diastereoisomers (2:2:1:1 ratio as determined by ^{1}H NMR): **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.49, 7.24, 7.18, and 7.06 (s, 1 H), 5.70-5.5.58 (m, 0.5 H), 5.47-5.5.30 (m, 0.5 H), 4.35-4.21 (m, 1 H), 3.74 (s, 3 H), 3.63-3.48 (m, 1 H), 2.60-2.36 (m, 1.5 H), 2.20-2.05 (m, 0.5 H), 2.02-1.33 (m, 15 H), 1.33-1.09 (m, 4 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 181.3, 181.0, 180.83, 180.77, 173.4, 173.3, 173.2, 155.63, 155.61, 155.5, 79.8, 79.7, 53.5, 53.4, 53.1, 52.5, 52.22, 52.18, 52.1, 51.9, 51.4, 36.9, 36.80, 36.78, 36.7, 36.11, 36.09, 35.8, 35.6, 35.40, 35.36, 35.13, 35.09, 32.3, 31.7, 31.6, 28.3, 21.9, 21.8, 21.7, 21.6, 16.3, 16.2, 16.1, 16.0; **IR** (CH_2Cl_2, cm^{-1}) 3227, 3056, 2976, 2932, 2870, 1739, 1688, 1501, 1456, 1391, 1366, 1266, 1165, 1050, 1024; **HRMS** (APCI) calculated for $C_{16}H_{28}N_2O_5Na$ [M+Na^+]: 351.1896, found: 351.1899.

6. Stern-Volmer Experiments

Rate of quenching (k_q) were determined using Stern–Volmer kinetics:

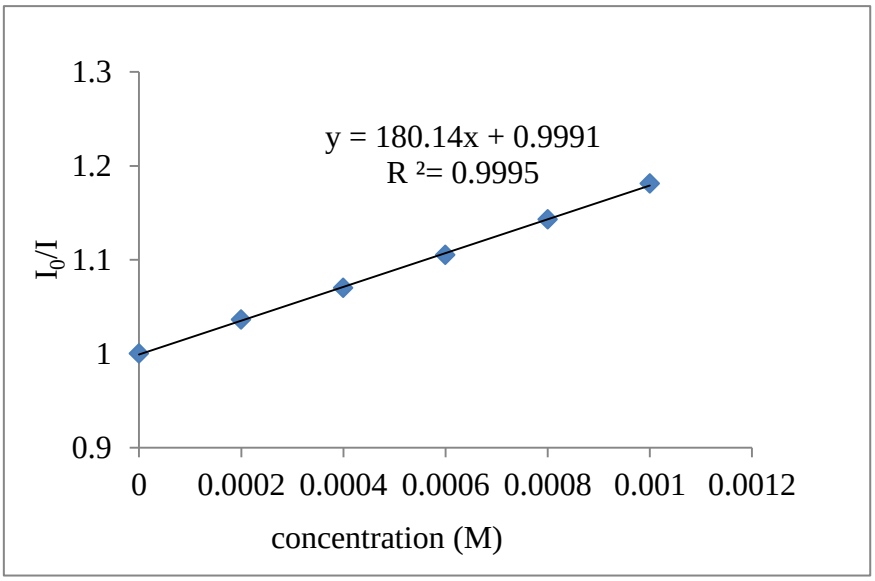
$$I_0/I = k_q\tau_0[\text{Quencher}]$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the lifetime of the photocatalyst (τ_0 = 2.3 × 10^{-6} s for $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in acetonitrile).[1]

Stern-Volmer luminescence quenching experiments were run with freshly prepared solutions of 1.0 × 10^{-6} M $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in DMF at room temperature. The solutions were irradiated at 380 nm and luminescence was measured at 470 nm. For each sample, the luminescence was acquired three times and averaged. Each sample was prepared twice and the averages of the results were used for the graphical representation. Linear regression of I_0/I against concentration of quencher to yield $k_q\tau_0$ is done in Microsoft Excel.

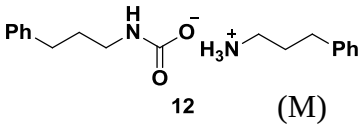
Supplementary Table 2. Fluorescence quenching $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ at variable concentrations of quinuclidine.

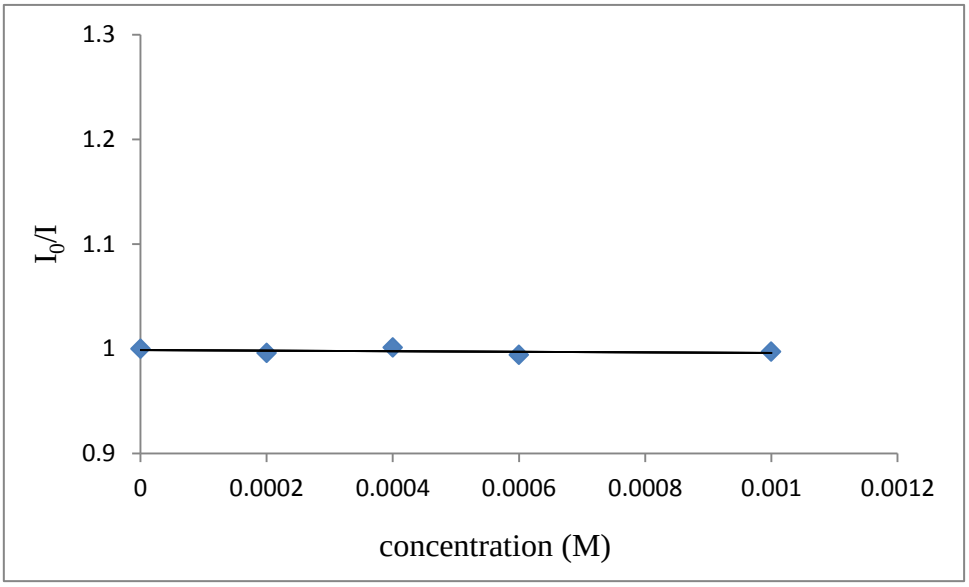
Quinuclidine (M)	0	0.0002	0.0004	0.0006	0.0008	0.001
I_0/I	1	1.036	1.070	1.105	1.143	1.181



Supplementary Fig. 2. Stern-Volmer plot of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ at variable concentrations of quinuclidine. $k_q = 7.83 \times 10^7\ M^{-1}\ s^{-1}$.

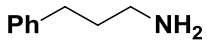
Supplementary Table 3. Fluorescence quenching Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 at variable concentrations of alkylammonium carbamate **12**.

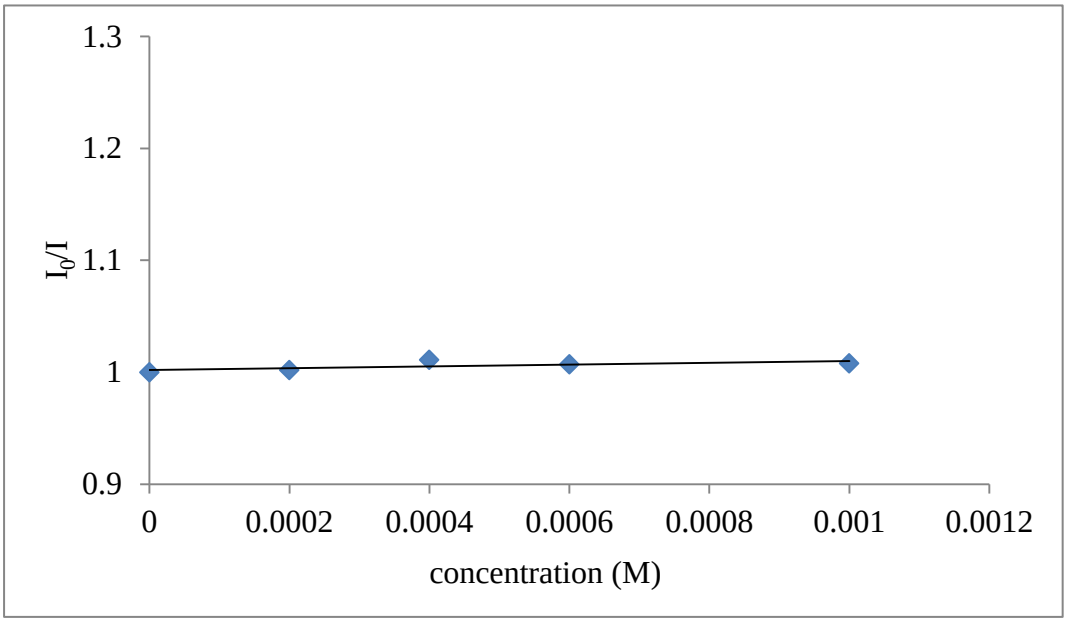
 12 (M)	0	0.0002	0.0004	0.0006	0.001
I_0/I	1	0.996	1.001	0.994	0.997



Supplementary Fig. 3. Stern-Volmer plot of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 at variable concentrations of alkylammonium carbamate **12**.

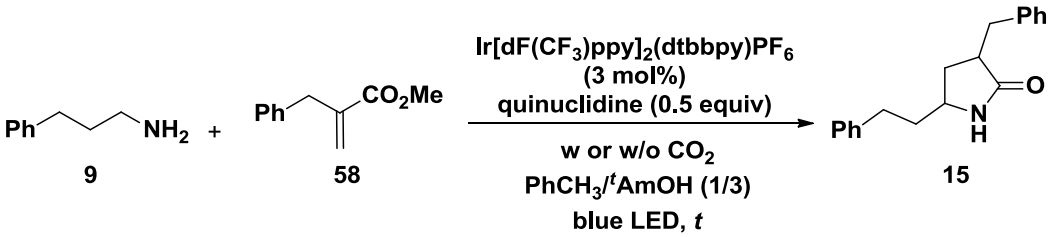
Supplementary Table 4. Fluorescence quenching Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 at variable concentrations of 3-phenyl-1-propylamine **9**.

 **9** (M)	0	0.0002	0.0004	0.0006	0.001
I_0/I	1	1.002	1.011	1.007	1.008



Supplementary Fig. 4. Stern-Volmer plot of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 at variable concentrations of 3-phenyl-1-propylamine **9**.

7. Kinetics Experiments



Typical procedure for reactions with CO_2: According to the **General Procedure A**, the reaction was carried out using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (6.6 mg, 0.006 mmol), quinuclidine (11.1 mg, 0.1 mmol), 3-phenyl-1-propylamine **9** (42.7 μL, 0.3 mmol), methyl 2-benzylacrylate **58** (35.2 mg, 0.2 mmol), and 0.5 mL of toluene and ^{t}AmOH mixture (1/3, v/v). The reaction was stopped after stirring for the indicated period of time. $CDCl_3$ (2 mL) and an internal standard (CH_2Br_2) were added to the reaction tube, conversion of methyl 2-benzylacrylate **58** was measured by ^{1}H NMR analysis of the crude reaction mixture. The crude reaction mixture was then concentrated *in vacuo* and the yield of product **15** was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. Each data point represents an average value determined from at least three separate experiments.

Supplementary Table 5. Determination of conversion of methyl 2-benzylacrylate **58** and yield of product **15** in the presence of CO_2.

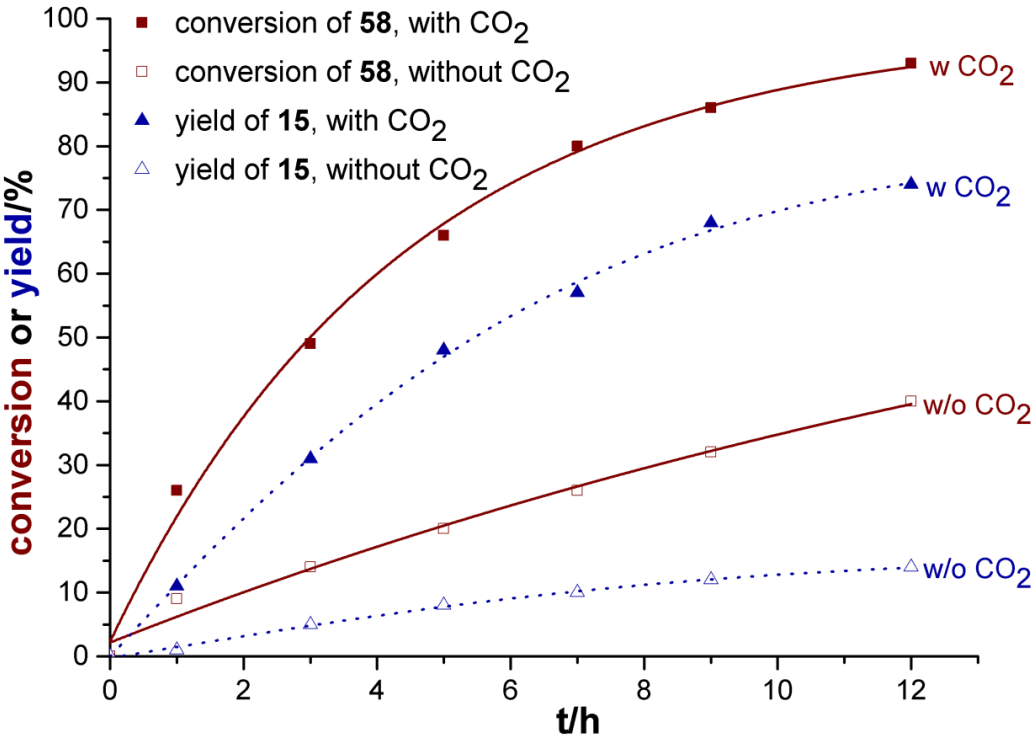
t/h	Conversion of **58**/%	Yield of **15**/%
0	0	0
1	26	11
3	49	31
5	66	48
7	80	57
9	86	68
12	93	74

Typical procedure for reactions *without* CO_2: To a 25-mL oven-dried Schlenk sealing tube containing a magnetic stir bar were added $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (6.6 mg, 0.006 mmol), quinuclidine (11.1 mg, 0.1 mmol), 3-phenyl-1-propylamine **9** (42.7 μL, 0.3 mmol), methyl 2-benzylacrylate **58** (35.2 mg, 0.2 mmol), and 0.5 mL of toluene and ^{t}AmOH mixture (1/3, v/v) in a glovebox under argon atmosphere. The reaction tube was sealed and taken out of the glovebox and placed approximately 3 inches away from a Kessil® LED illuminator. The reaction was stopped after stirring for the indicated period of time. $CDCl_3$ (2 mL) and an internal standard (CH_2Br_2) were added to the reaction tube, conversion of methyl 2-benzylacrylate **58** was measured by ^{1}H NMR analysis of the crude reaction mixture. The crude reaction mixture was then concentrated *in vacuo* and the yield of product **15** was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. Each data point represents an average value determined from at least three separate experiments.

For the reactions without CO_2, *N*-alkylation (aza-Michael addition) product methyl 2-benzyl-3-((3-phenylpro-pyl)-amino)propanoate **59** was detected by UPLC-MS as the major product, however, the yield of **59** was not calculated due to signal overlap of the crude ^{1}H NMR spectra. 2-Benzyl-3-((3-phenylpro-pyl)-amino)propanoate **59** was isolated as a colorless oil: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.31-7.24 (m, 4 H), 7.24-7.14 (m, 6 H), 3.64 (s, 3 H), 3.01-2.94 (m, 1 H), 2.92-2.84 (m, 2 H), 2.84-2.78 (m, 1 H), 2.75-2.67 (m, 1 H), 2.66-2.54 (m, 4 H), 1.81-1.73 (m, 2 H), 1.50 (brs, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 175.2, 142.1, 138.9, 128.8, 128.4, 128.33, 128.26, 126.4, 125.7, 51.6, 50.7, 49.1, 47.8, 36.3, 33.4, 31.5; **IR** (CH_2Cl_2, cm^{-1}) 3061, 3027 2930, 2854, 1730, 1603, 1495, 1453, 1436 1370, 1265, 1203, 1164, 1128, 1030; **HRMS** (ASAP) calculated for $C_{20}H_{26}NO_2$ [$M+H^+$]: 312.1964, found: 312.1970.

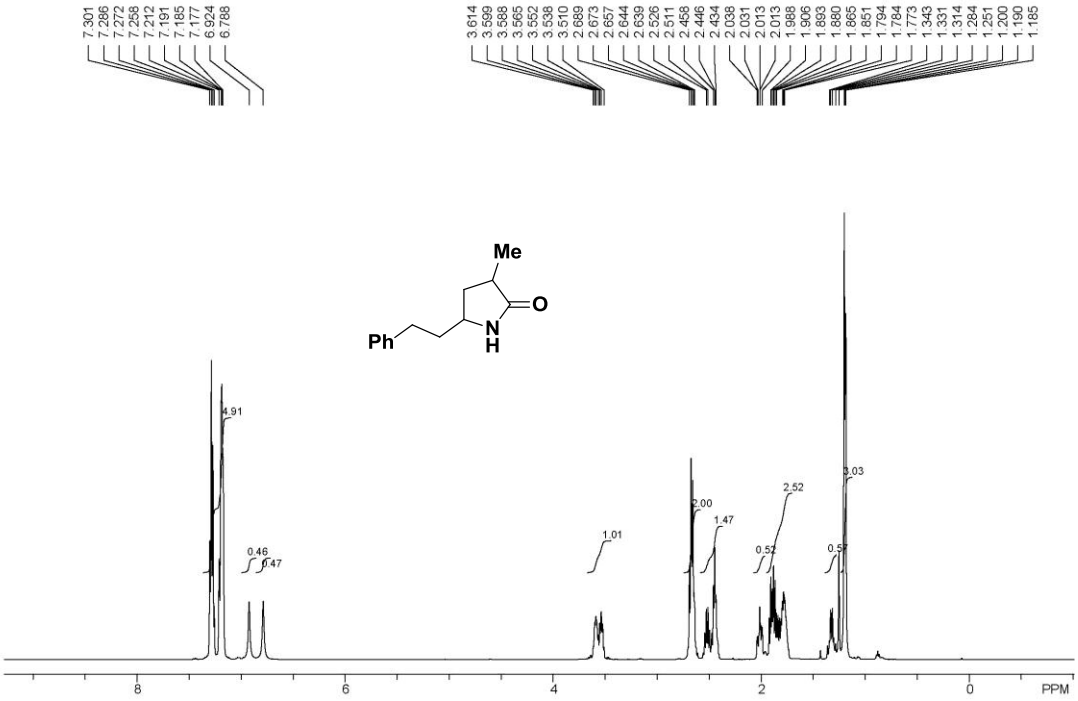
Supplementary Table 6. Determination of conversion of methyl 2-benzylacrylate **58** and yield of product **15** in the absence of CO_2.

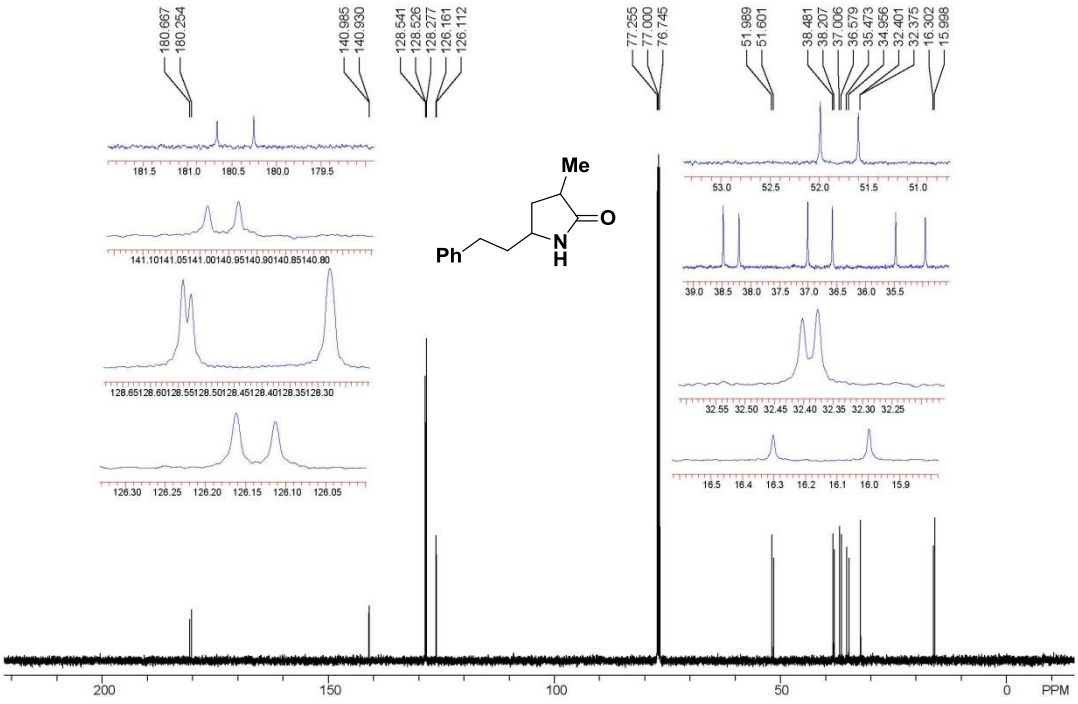
t/h	Conversion of **58**/%	Yield of **15**/%
0	0	0
1	9	1
3	14	5
5	20	8
7	26	10
9	32	12
12	40	14

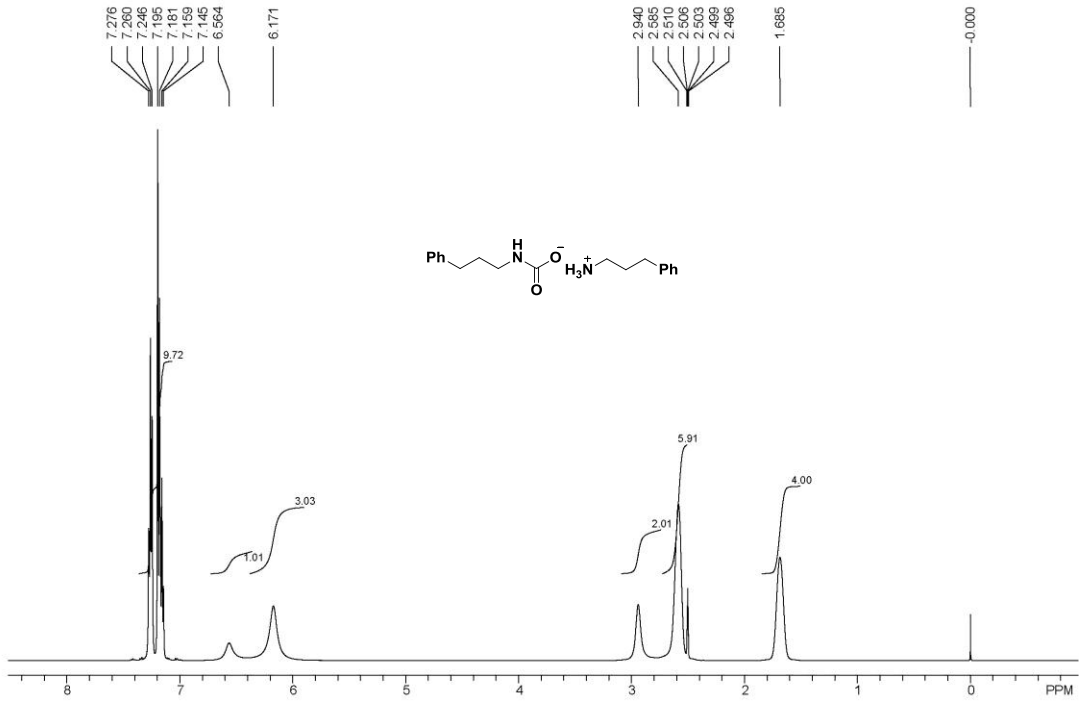


Supplementary Fig. 5. A comparison of acrylate consumption and product formation in the presence and absence of CO_2**.**

8. NMR Spectra



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7.145
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6.171
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2.510
2.506
2.503
2.499
2.496
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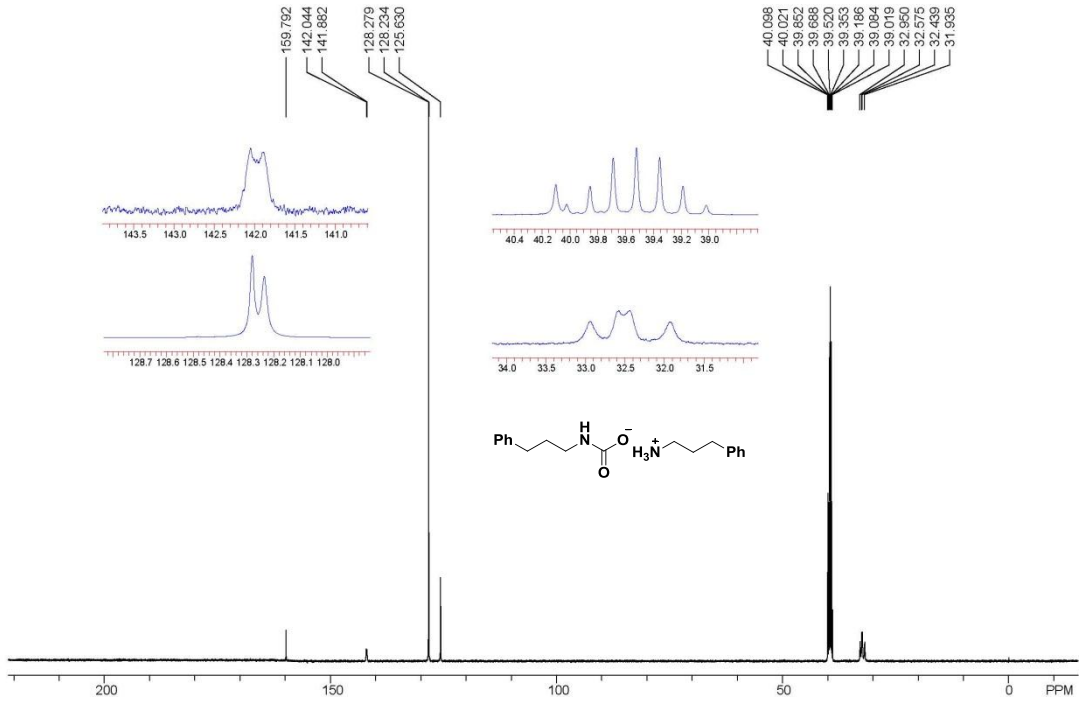
1.01
5.91
2.01
4.00
Ph
Ph
PPM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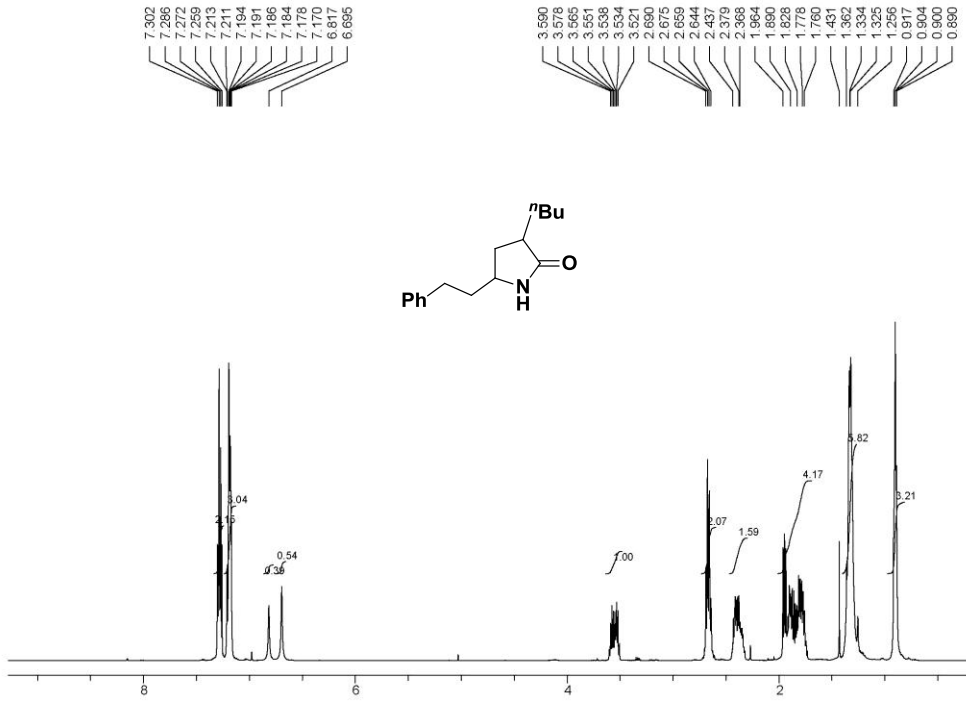
32.575
32.439
31.935
Ph
Ph
PPM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7.178
7.170
6.817
6.695
3.590
3.578
3.565
3.551
3.538
3.534
3.521
2.690
2.675
2.659
2.644
2.437
2.379
2.368
1.964
1.890
1.828
1.778
1.760
1.431
1.362
1.334
1.325
1.256
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0.904
0.900
0.890
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O
N
H
Ph
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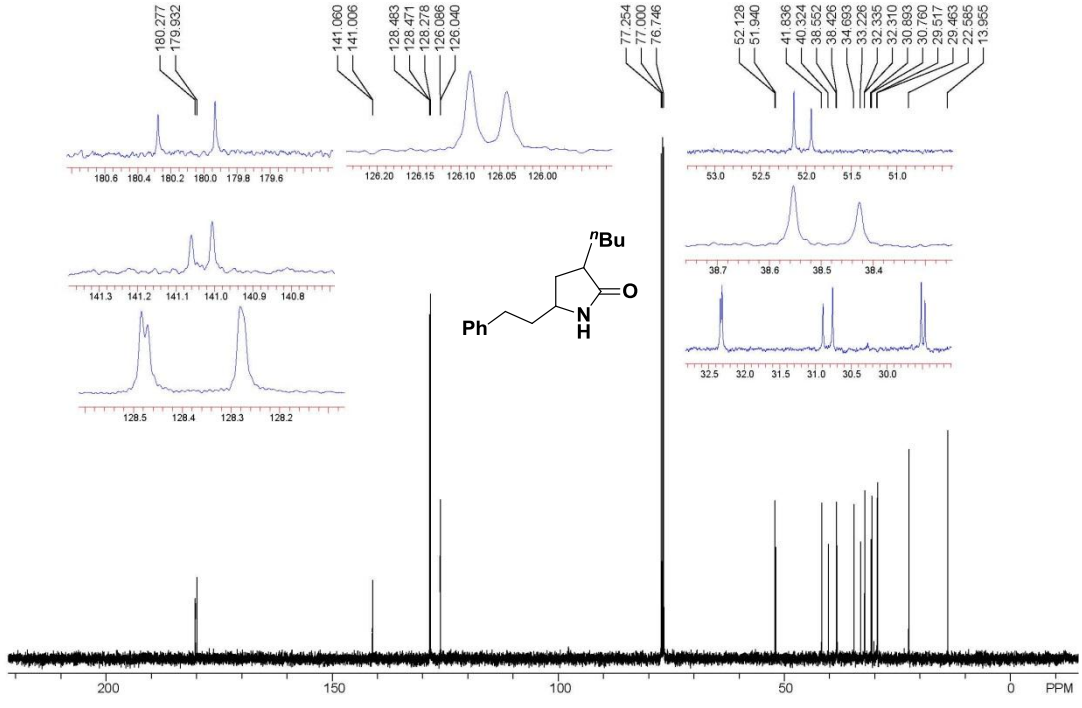
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77.000
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52.128
51.940
41.836
40.324
38.552
38.426
34.693
33.226
32.335
32.310
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H
Ph
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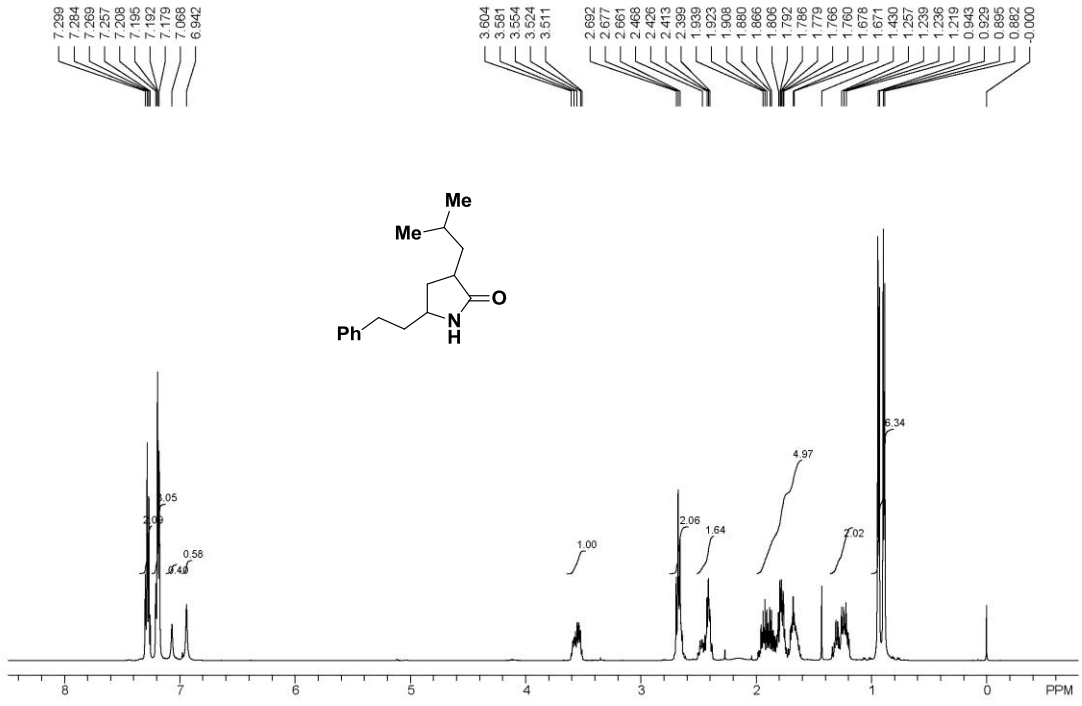
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3.524
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2.692
2.677
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1.923
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1.779
1.766
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1.678
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1.236
1.219
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0.929
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Me
O
N
H
Ph
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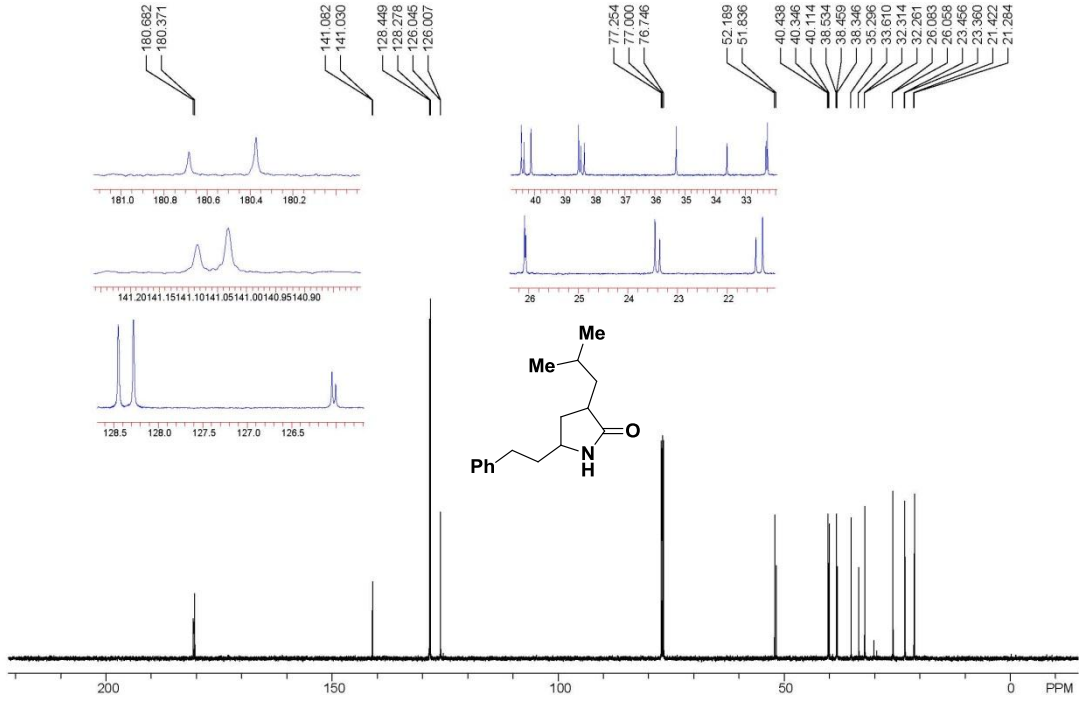
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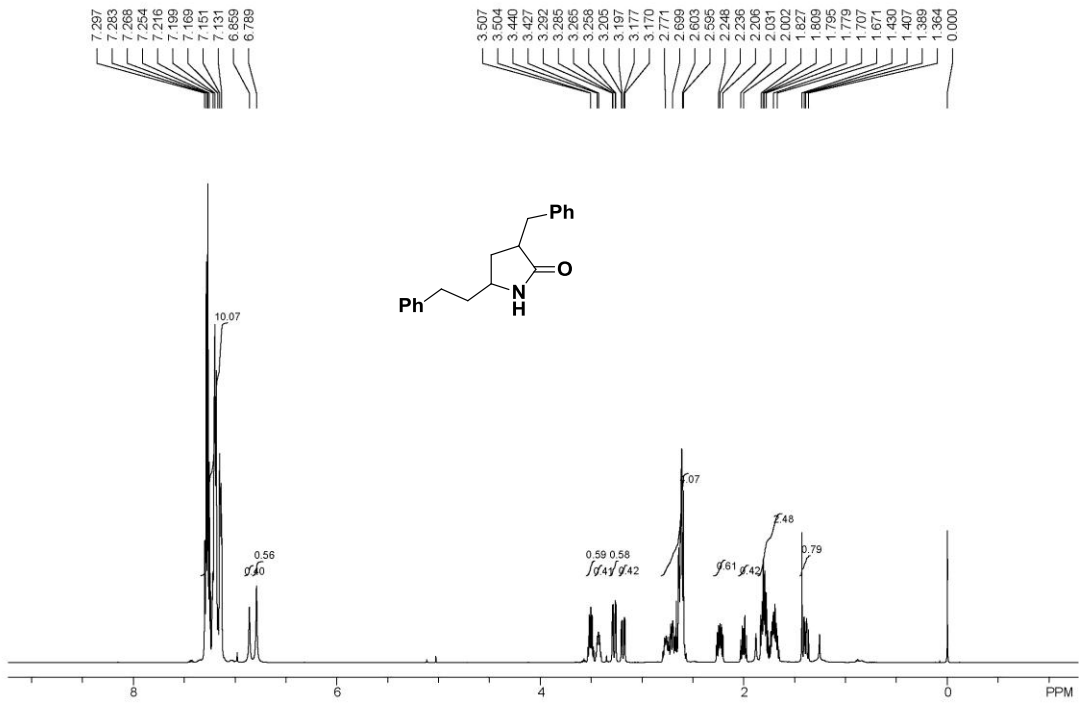
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3.504
3.440
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3.292
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3.205
3.197
3.177
3.170
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N
H
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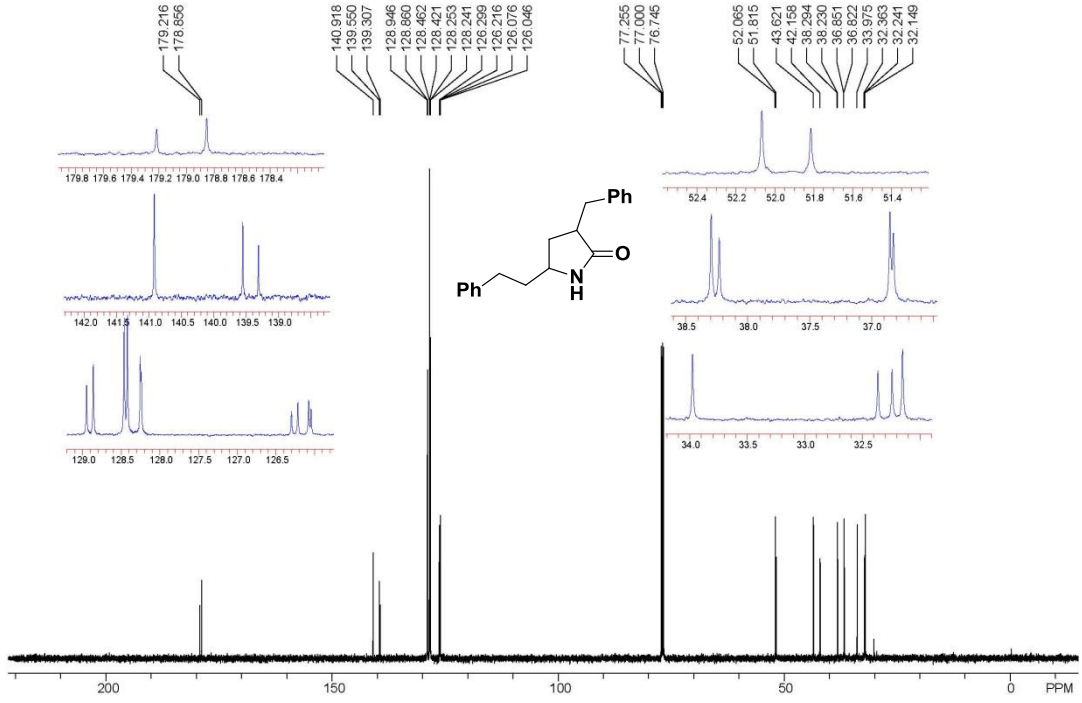
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126.216
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126.046
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52.065
51.815
43.621
42.158
38.294
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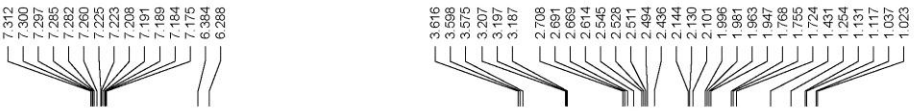
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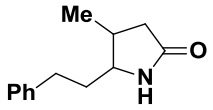
1.023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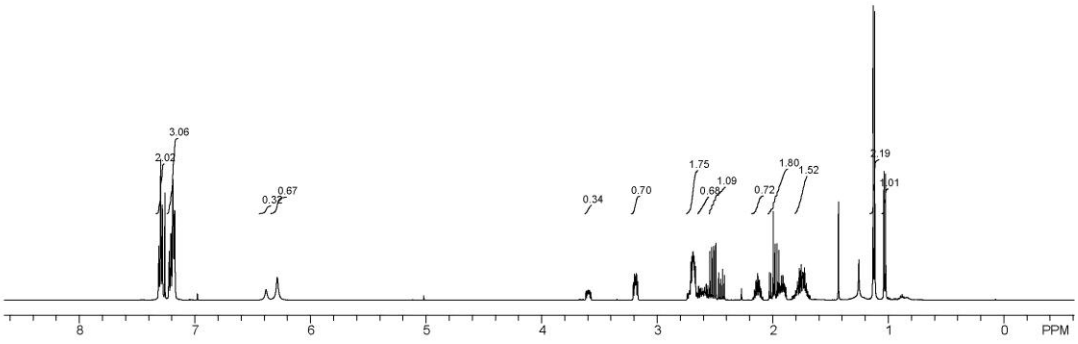
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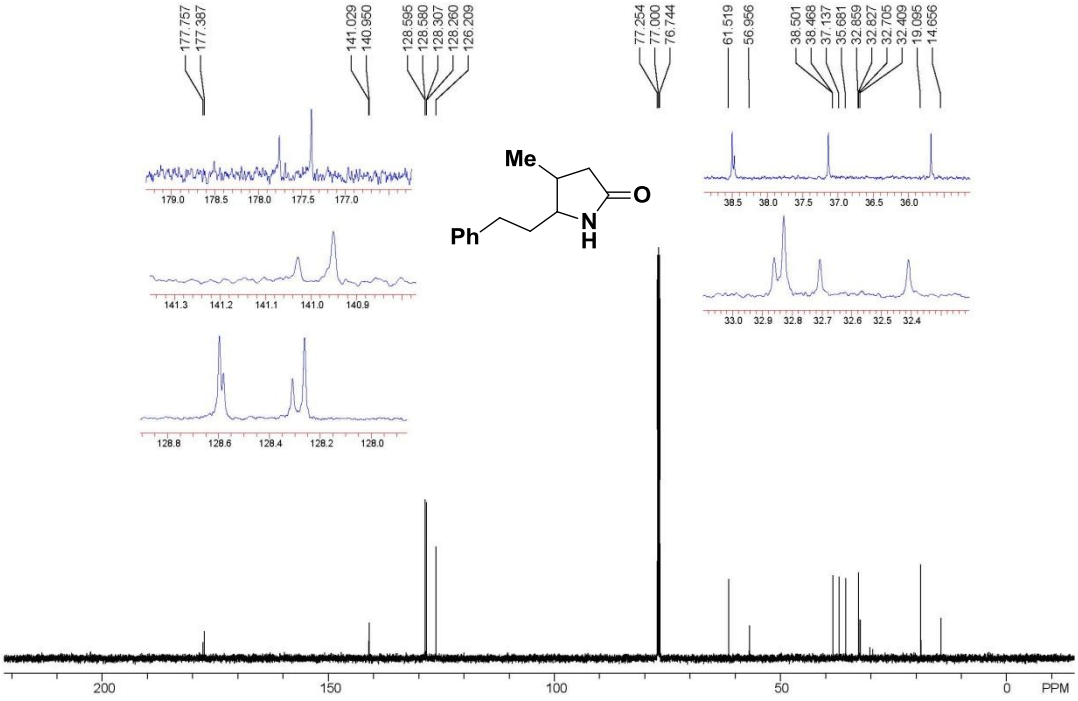
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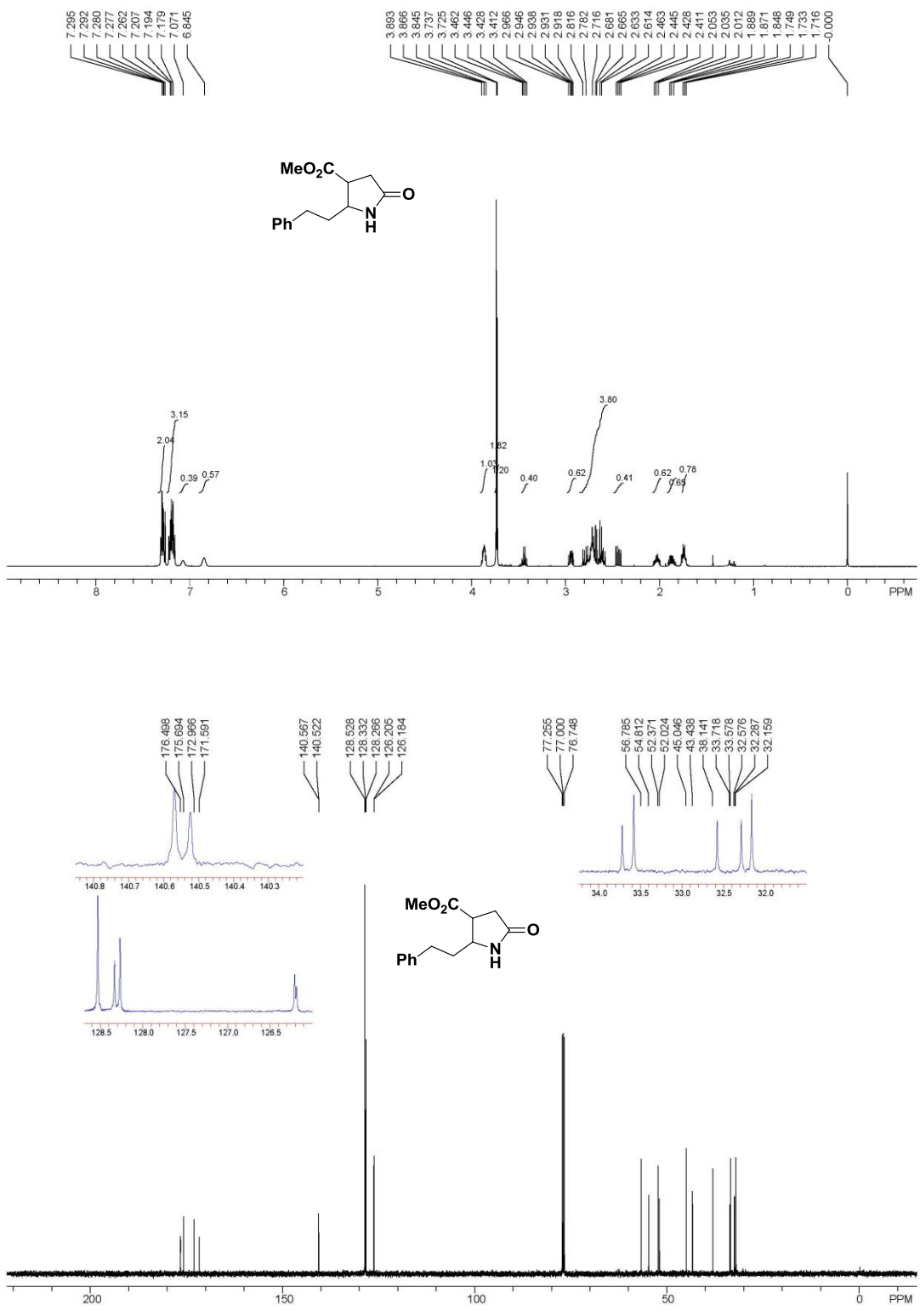
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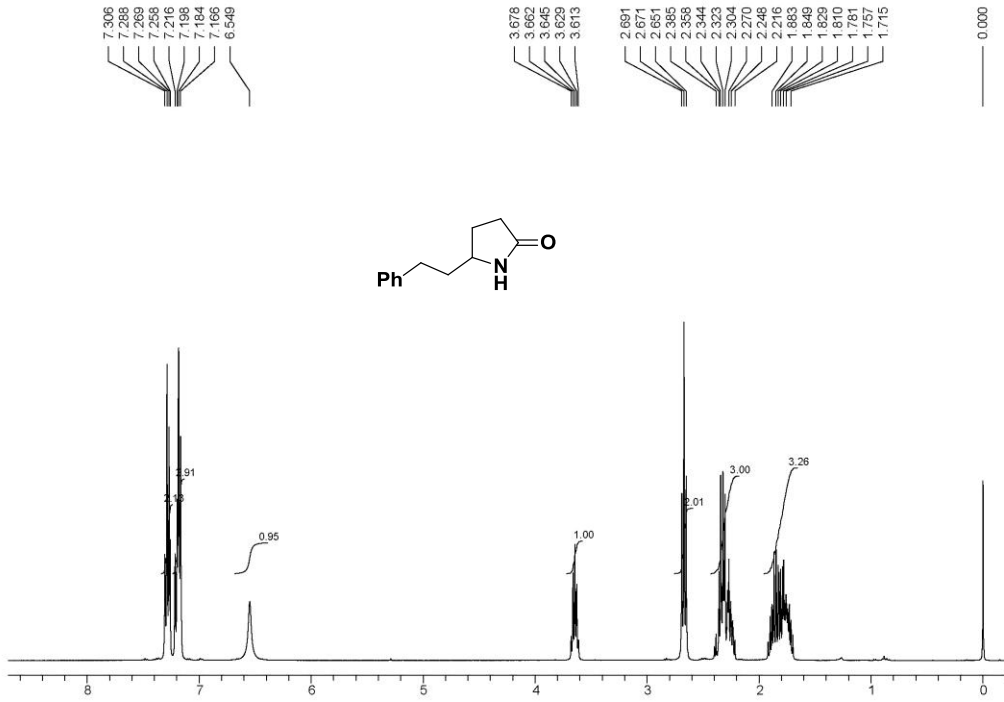
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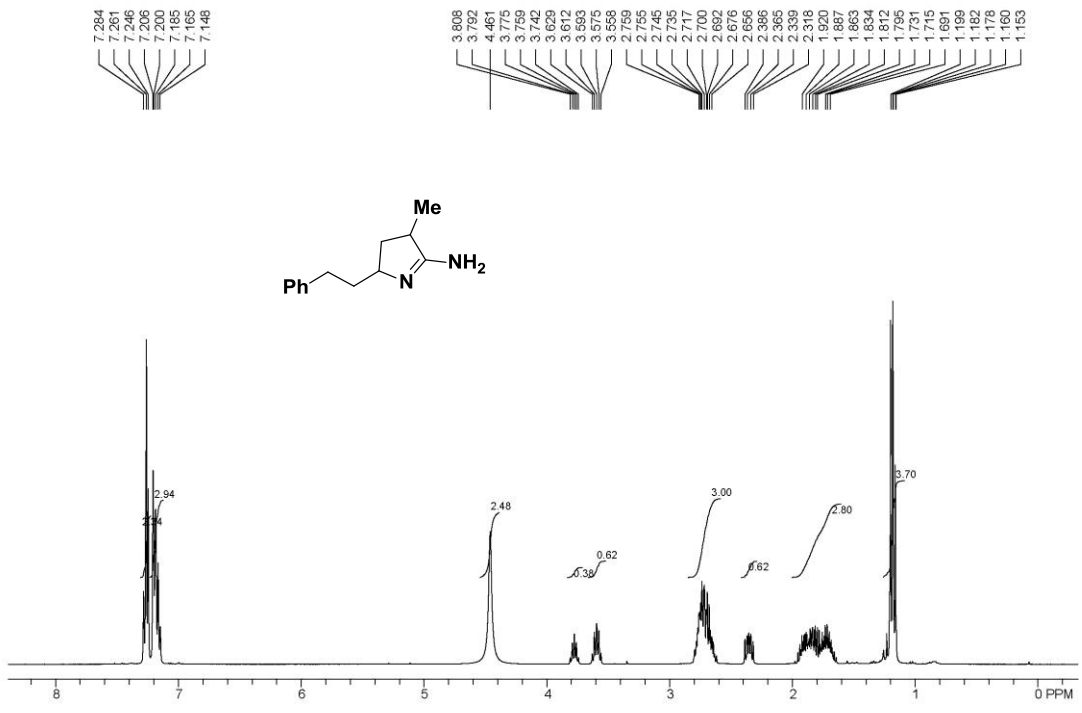
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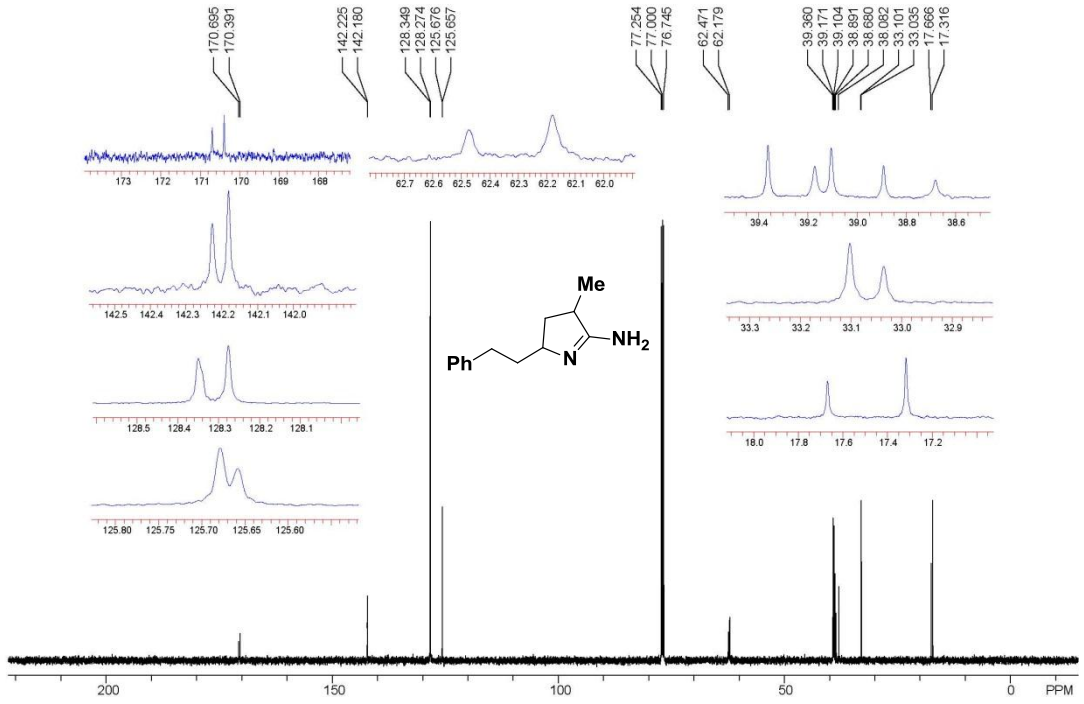
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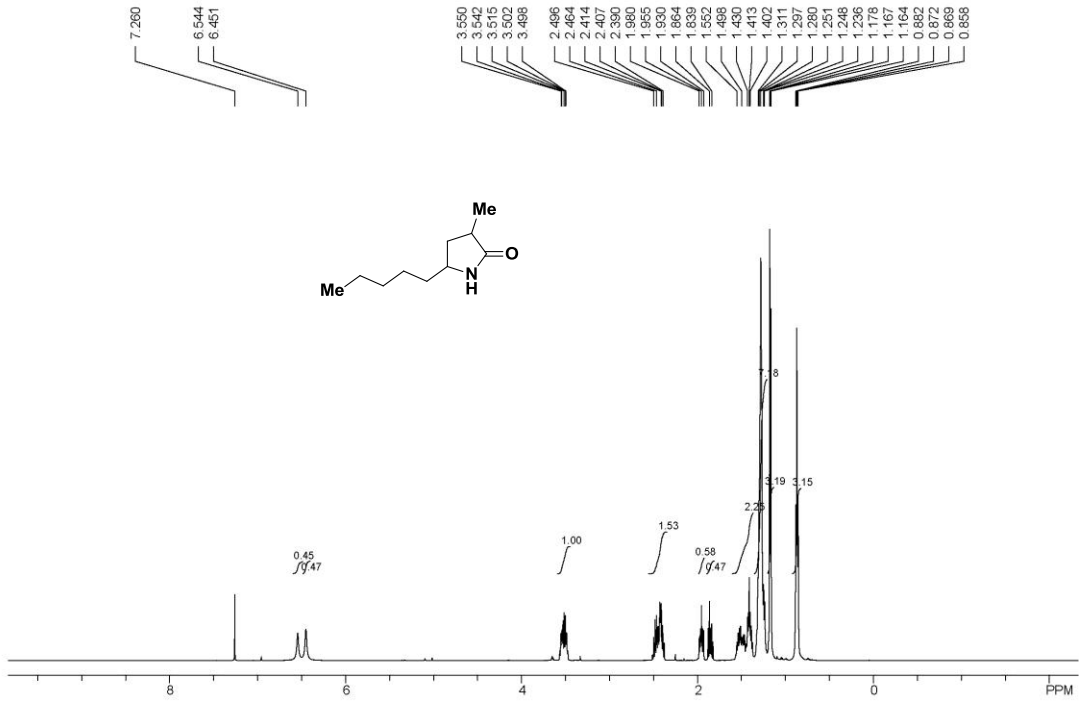
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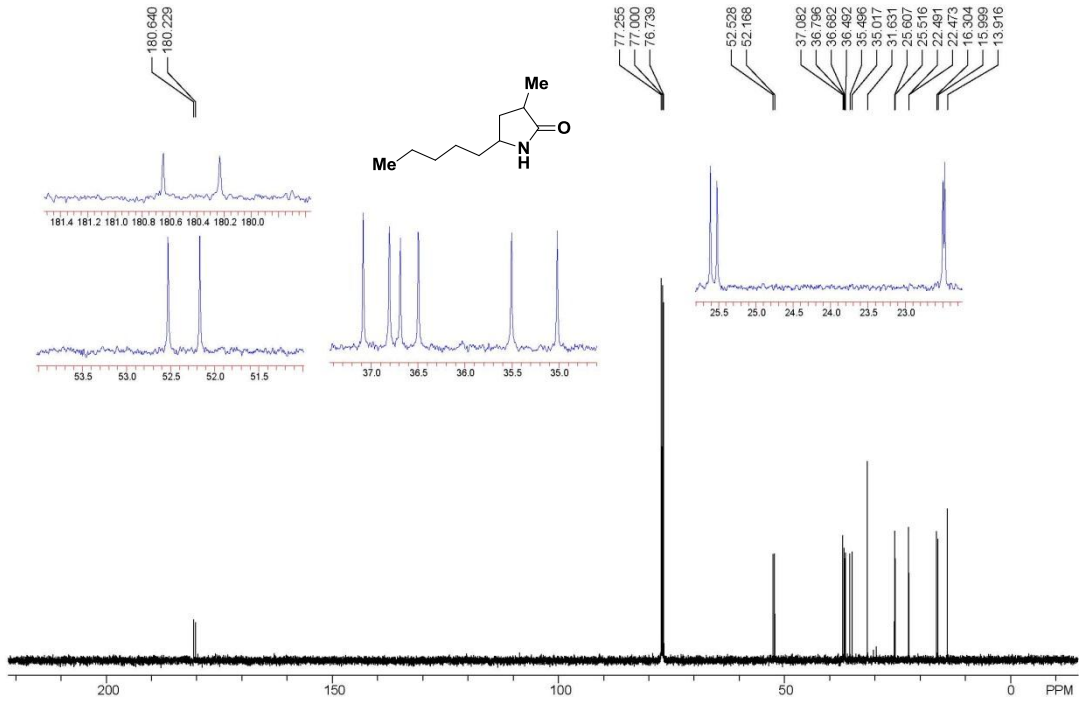
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25.516
22.491
22.473
16.304
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13.916
Me
O
N
H
Me
181.4 181.2 181.0 180.8 180.6 180.4 180.2 180.0
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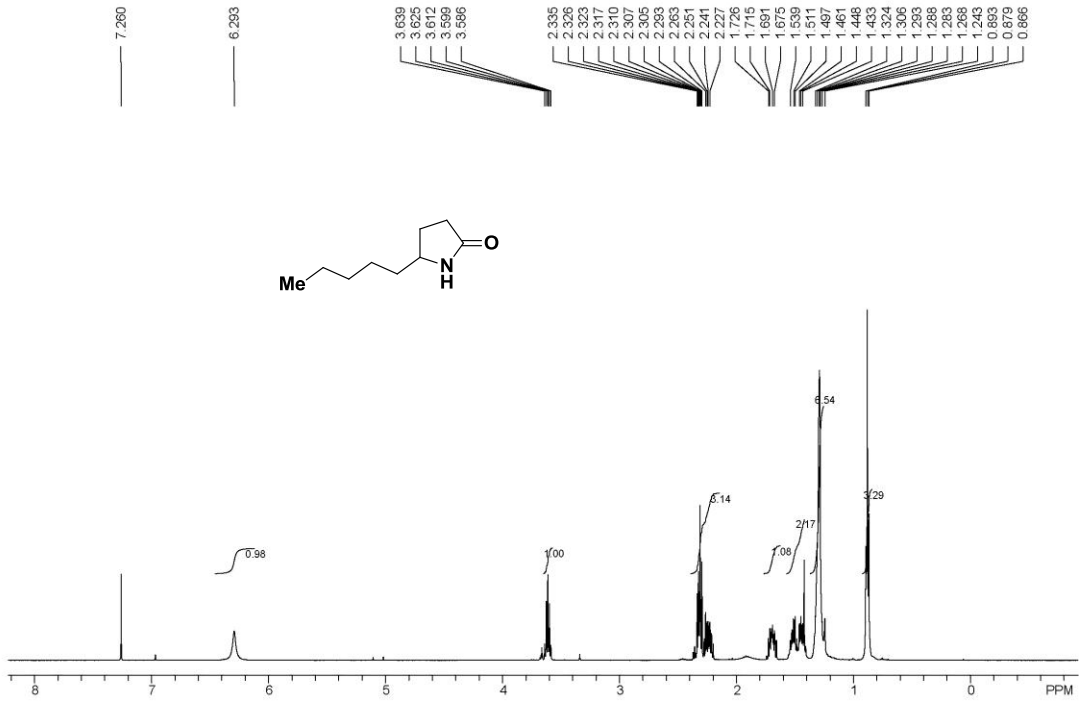
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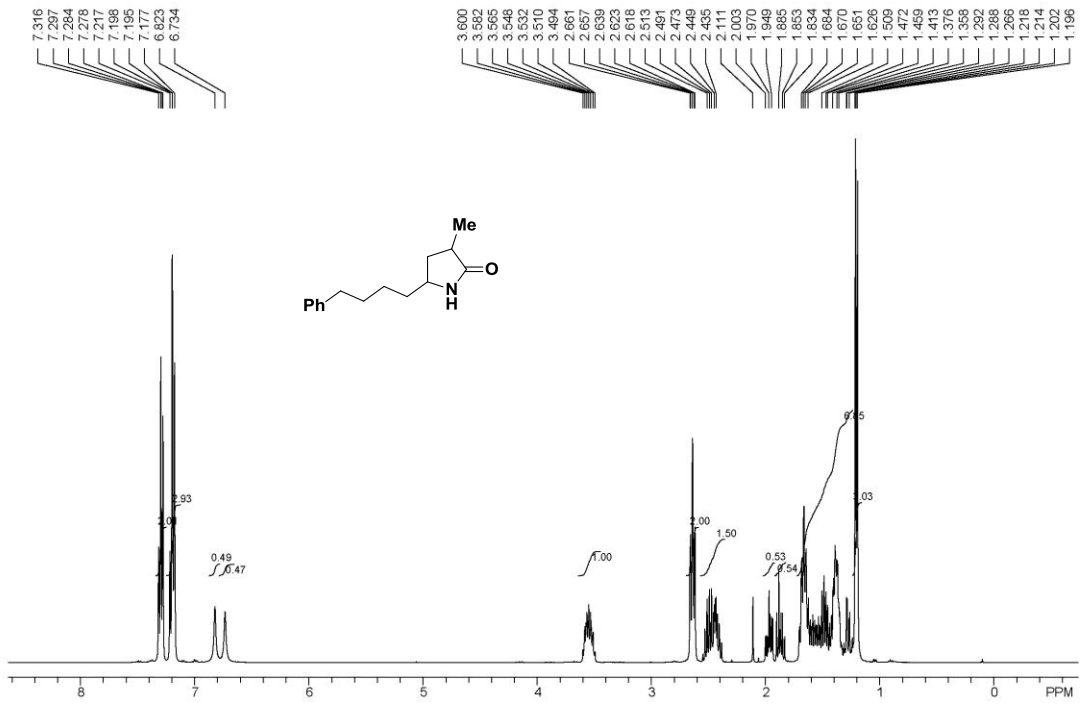
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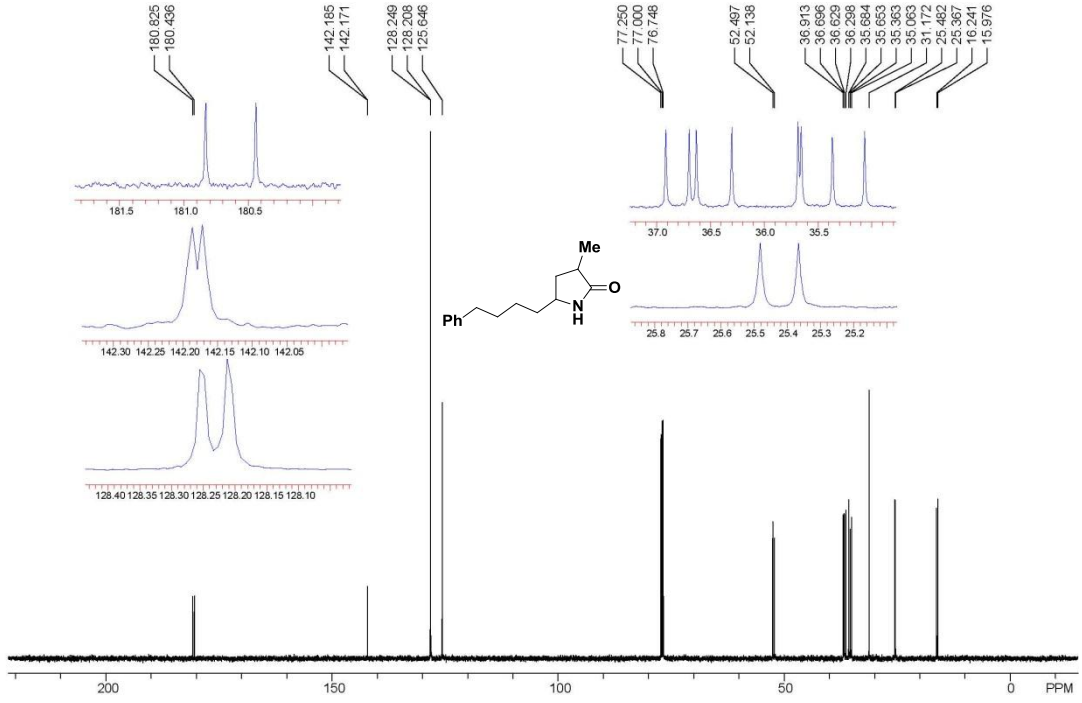
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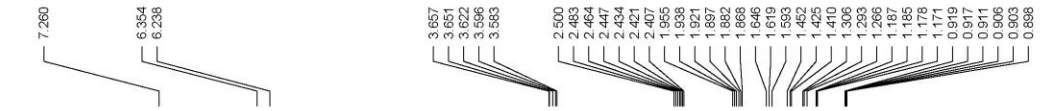
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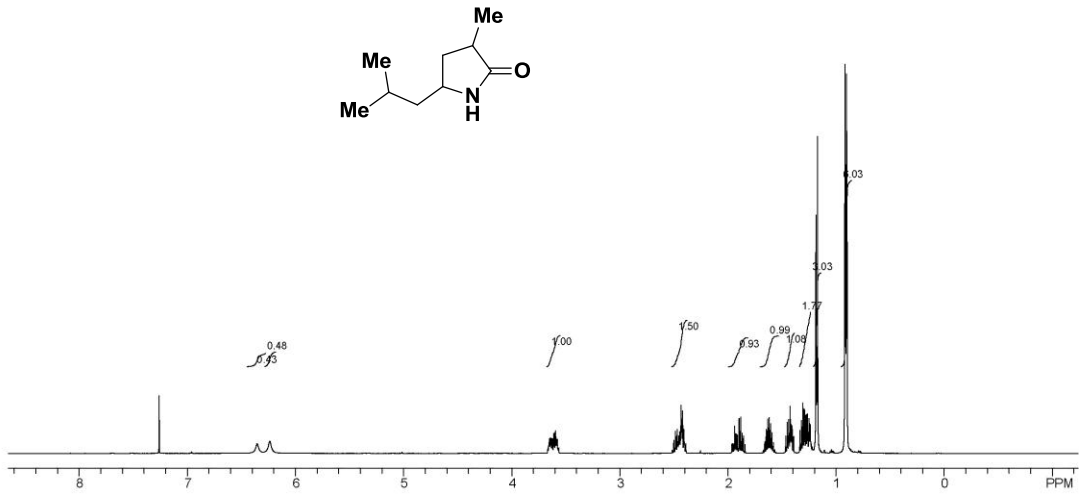
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6
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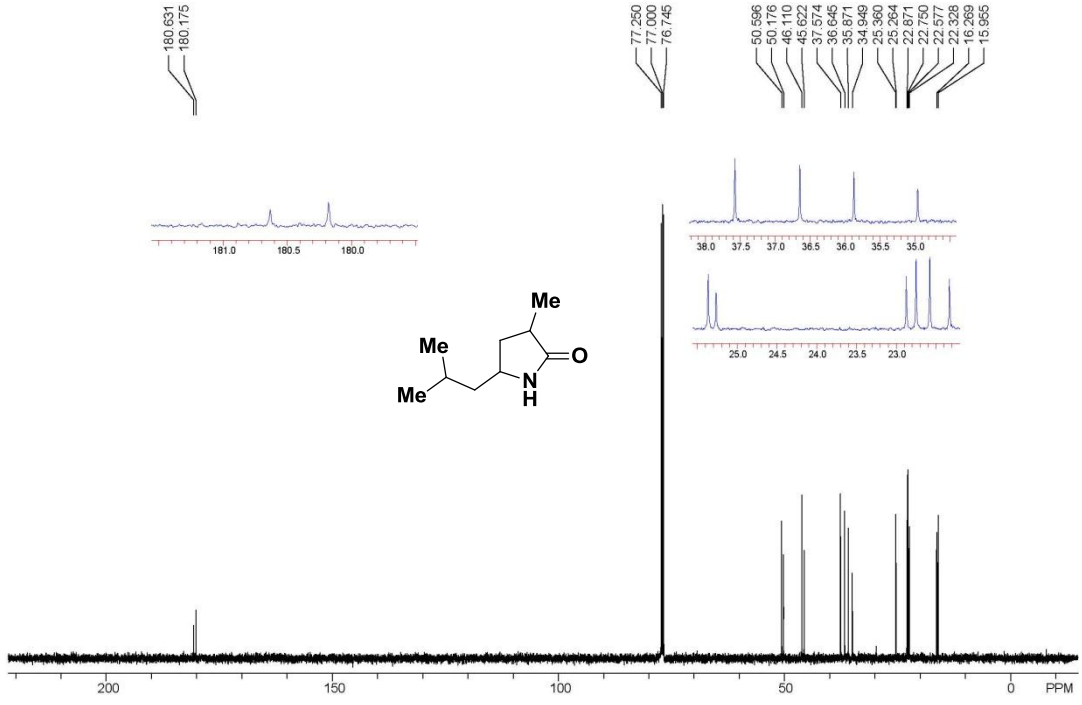
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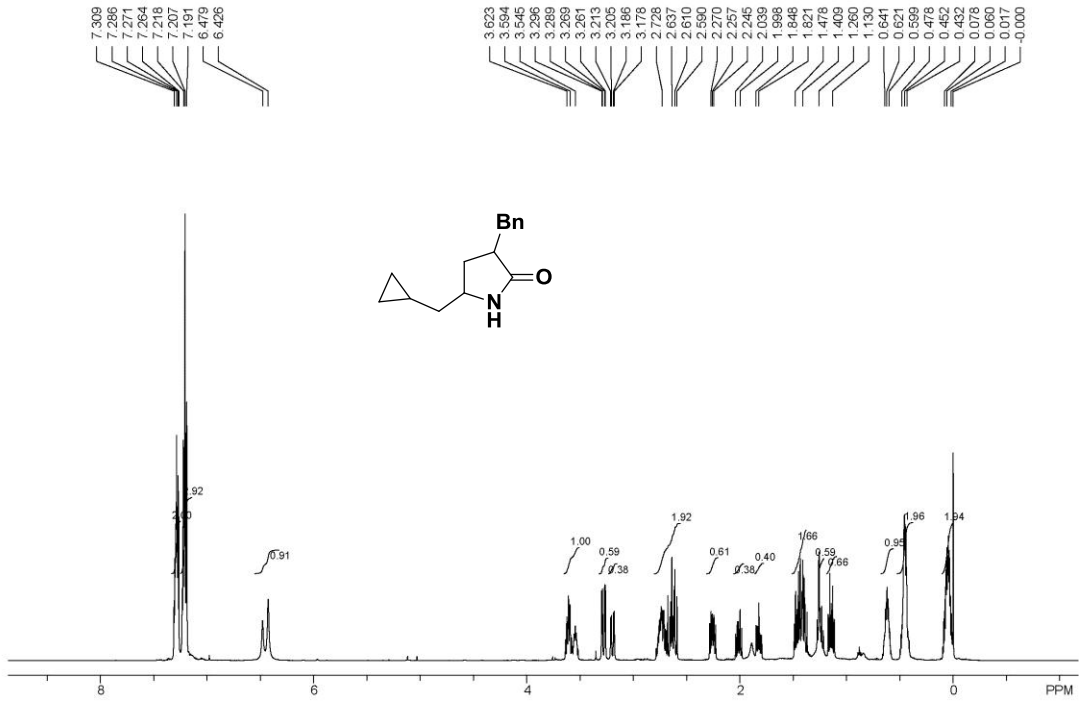
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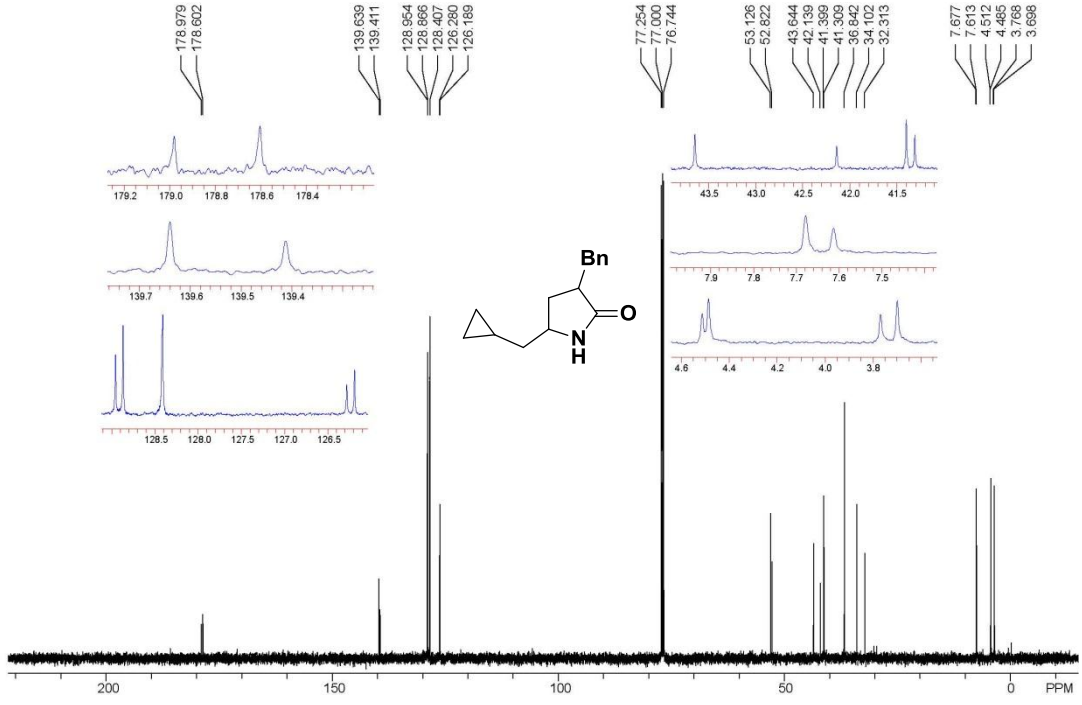
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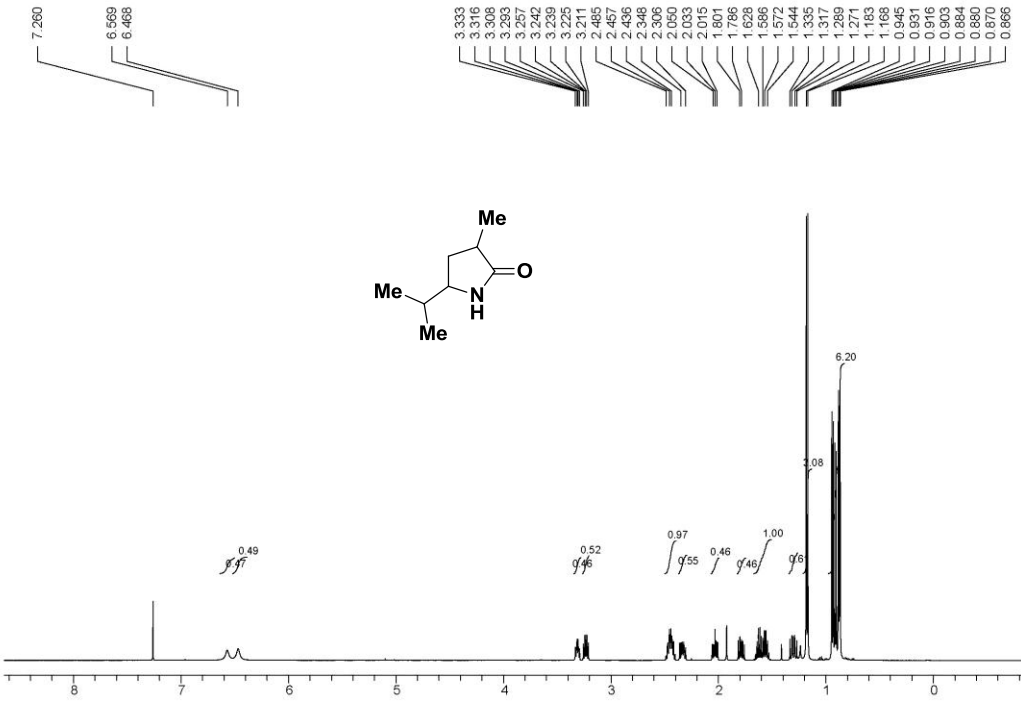
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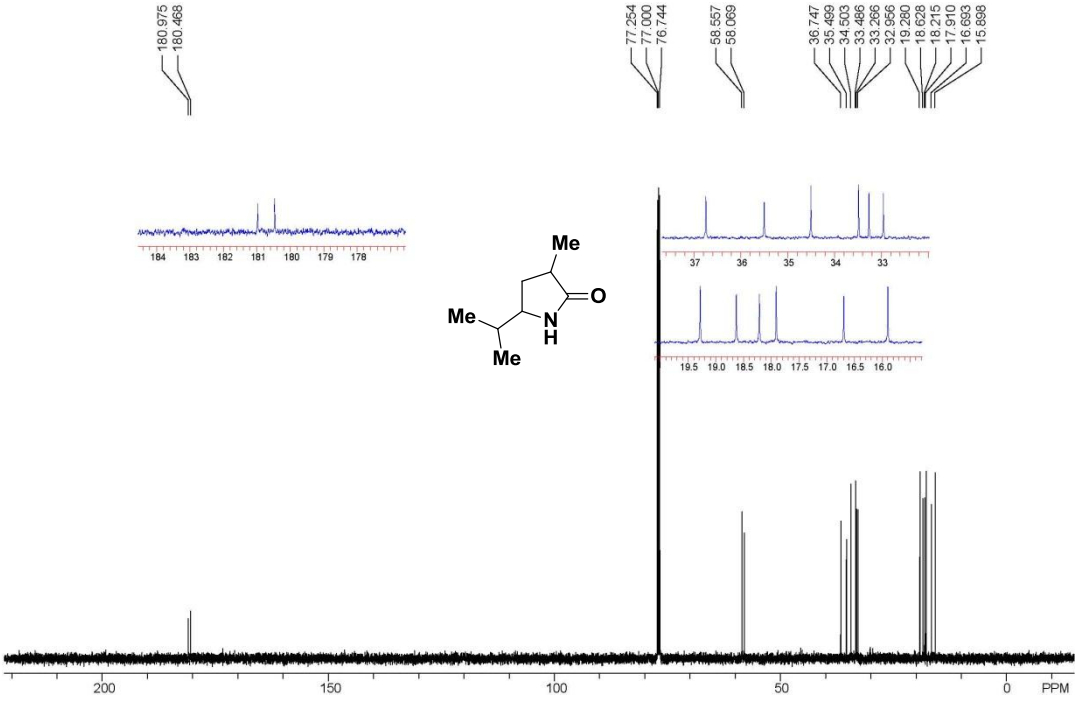
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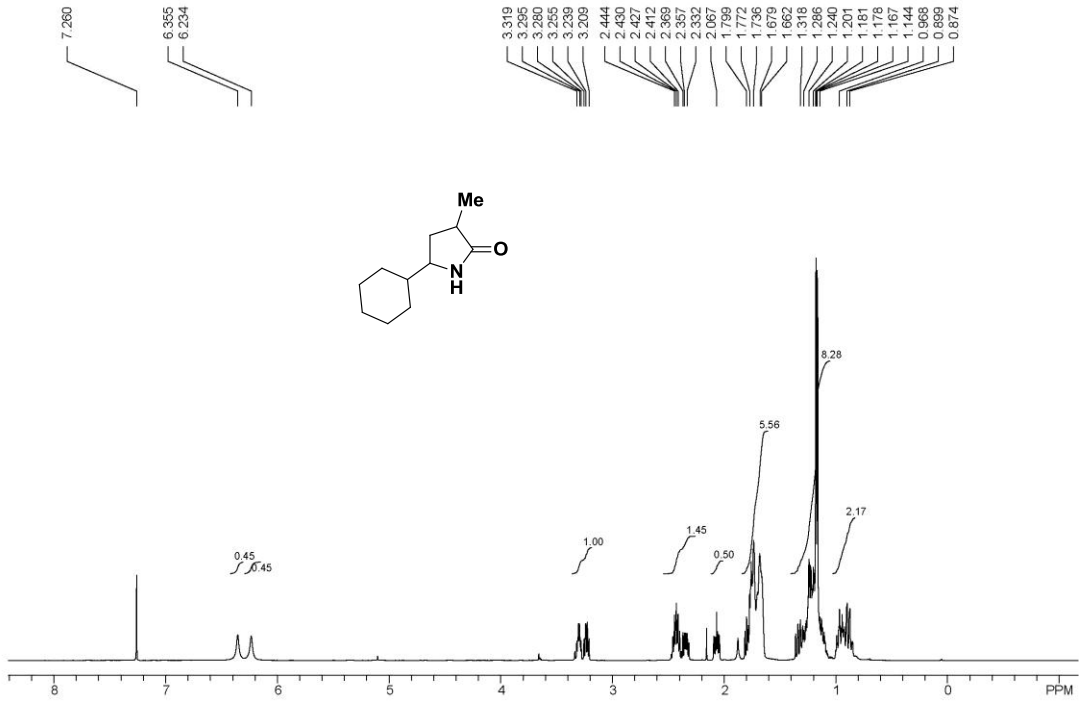
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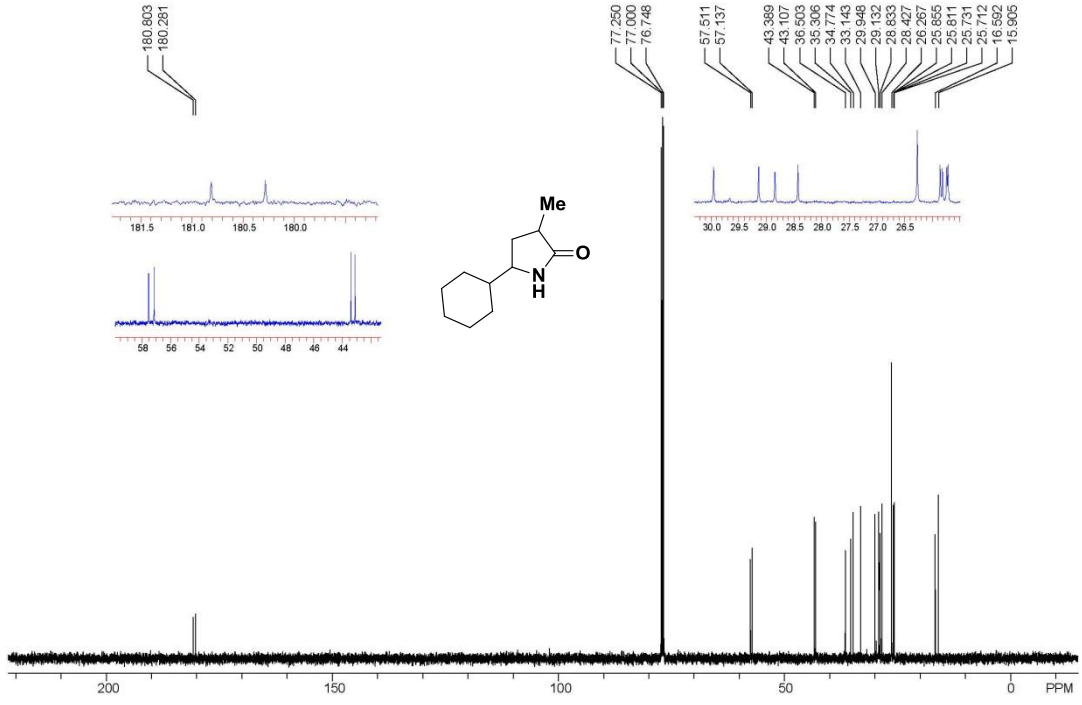
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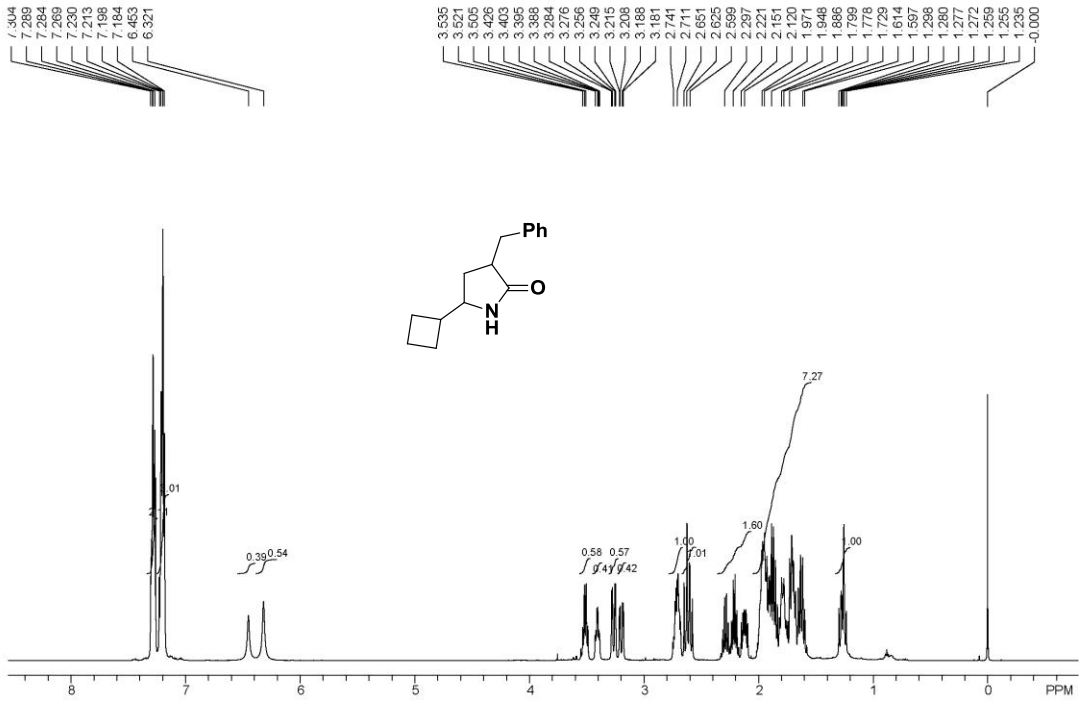
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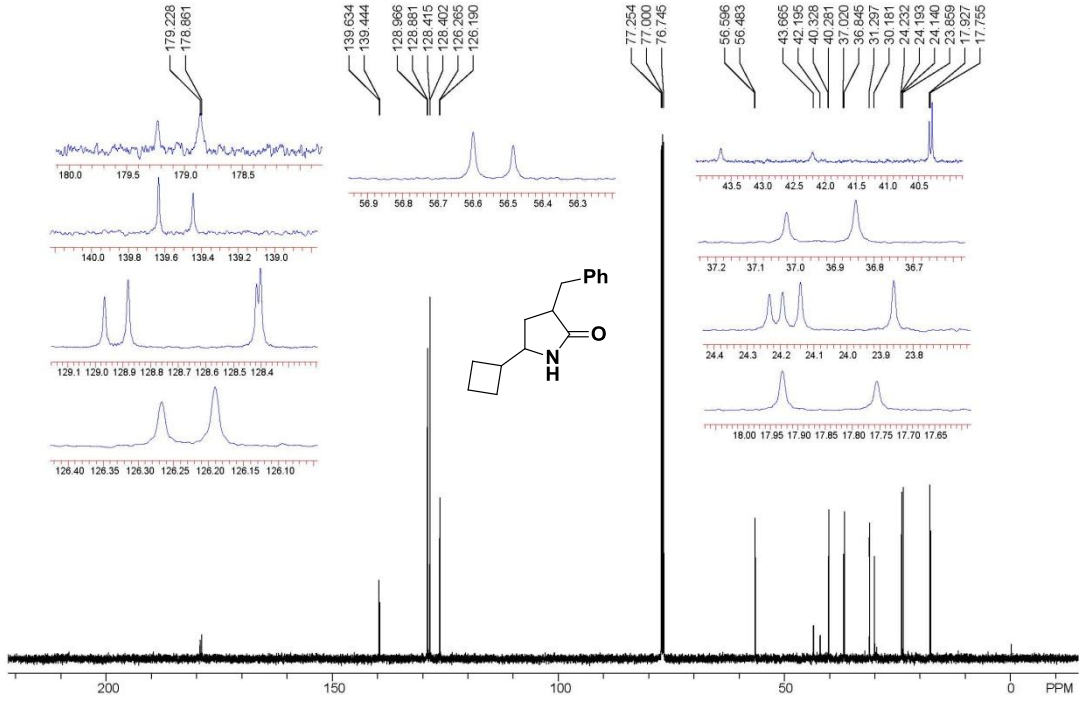
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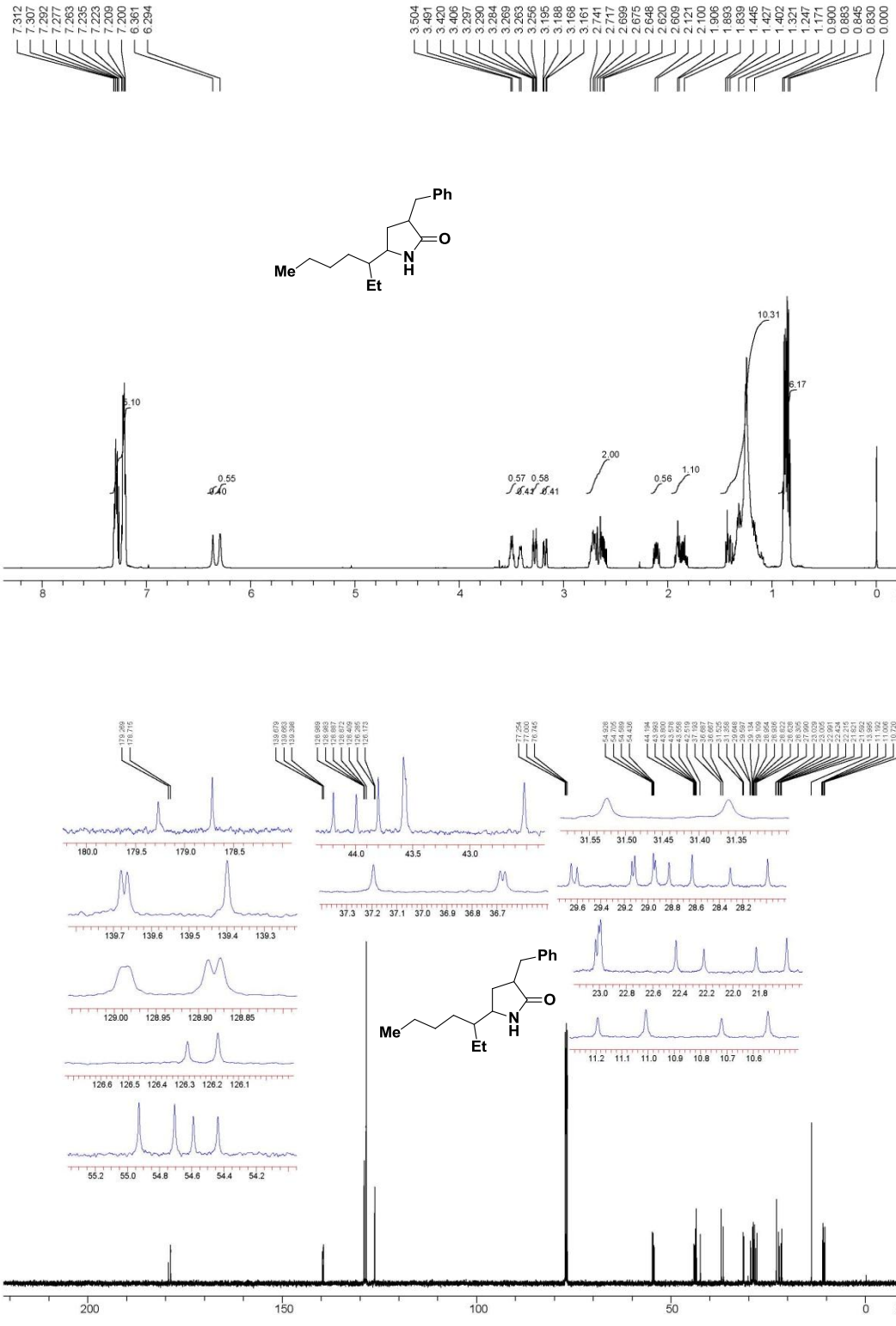
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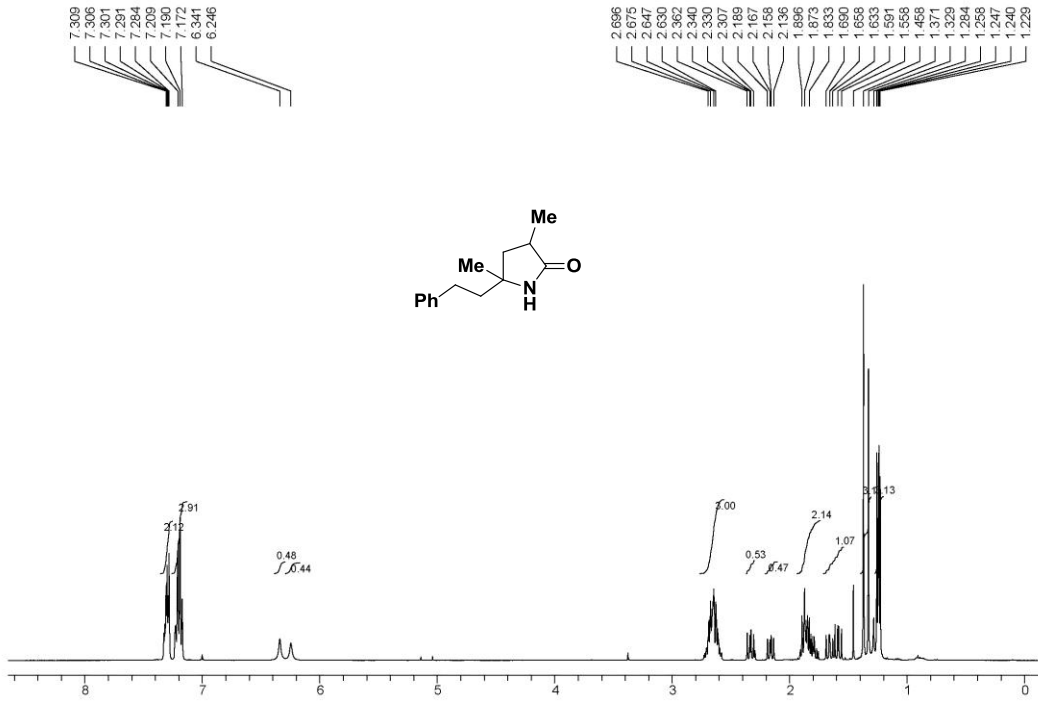
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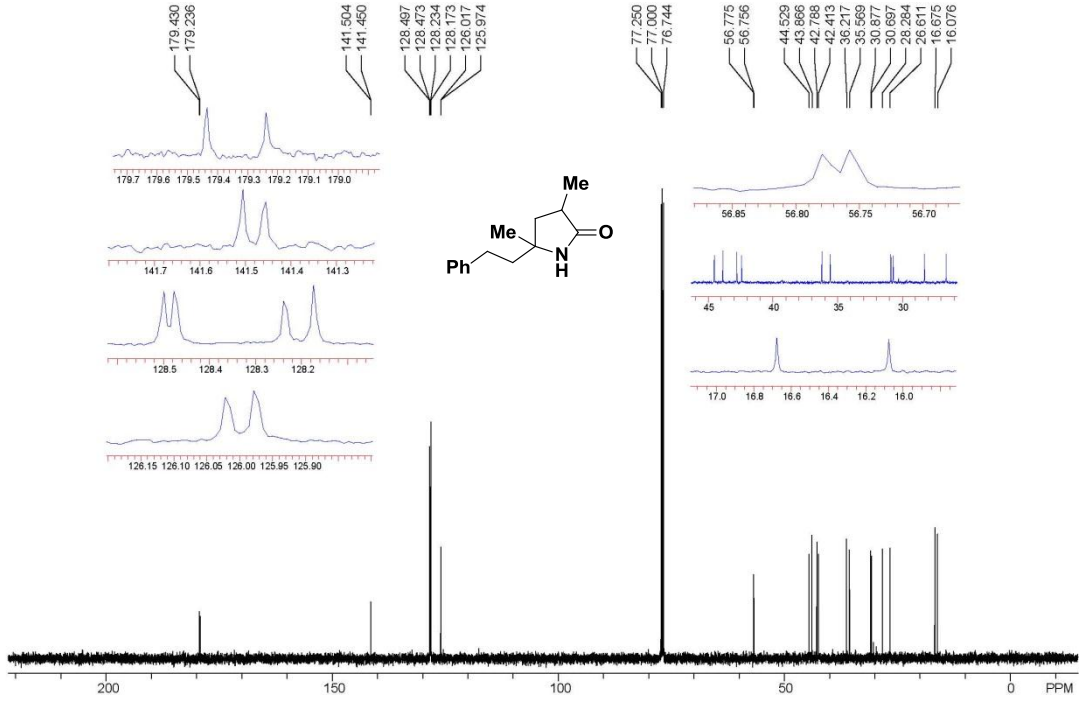
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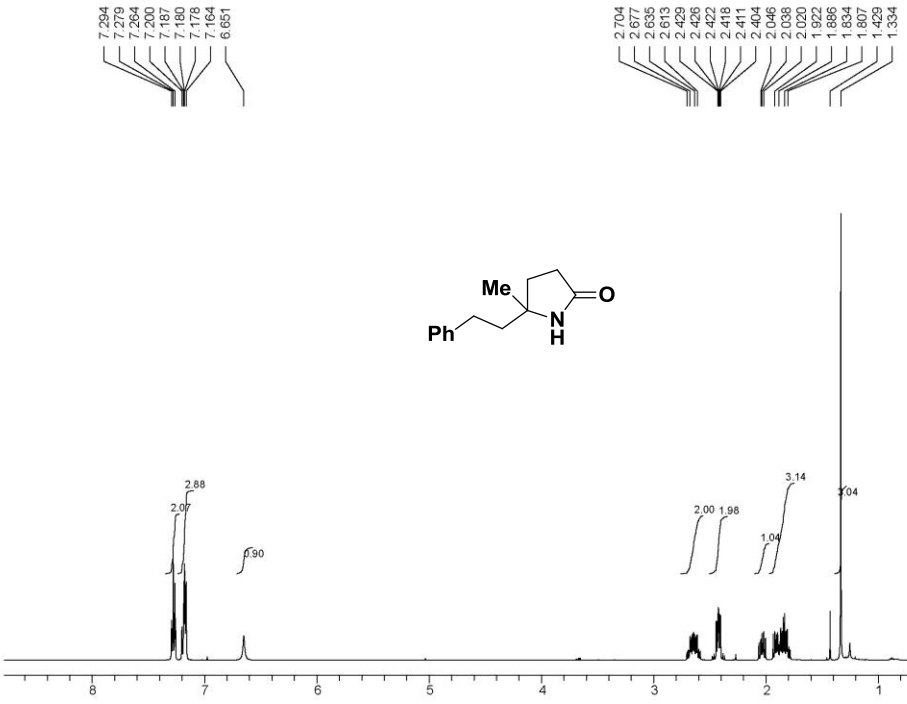
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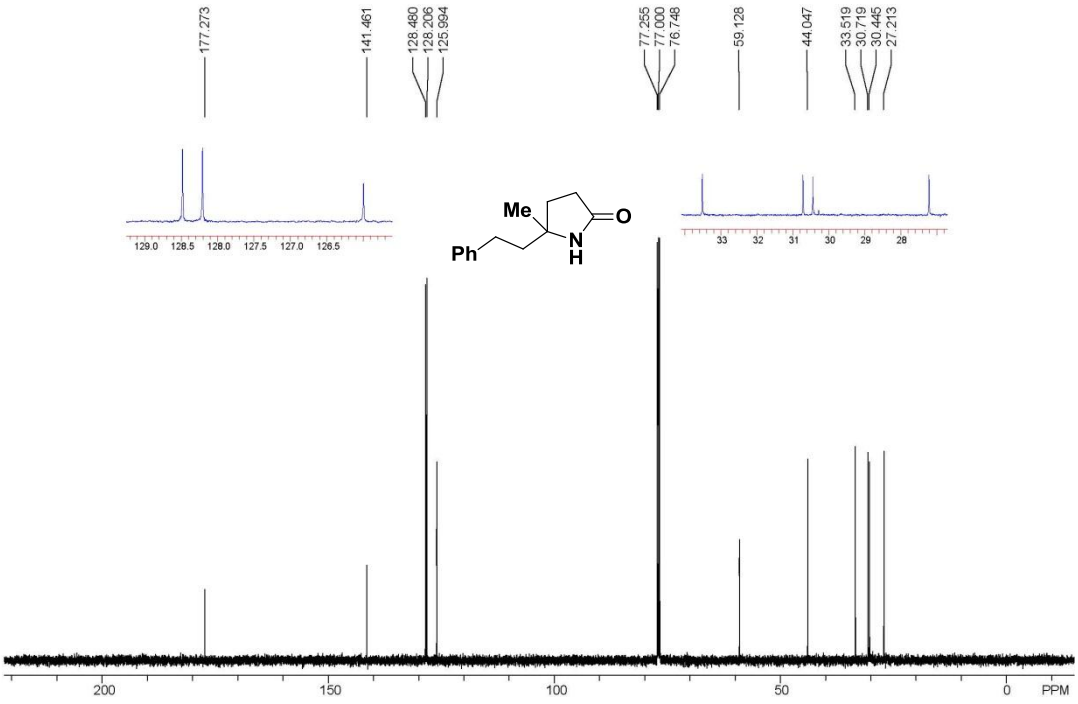
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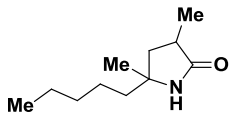
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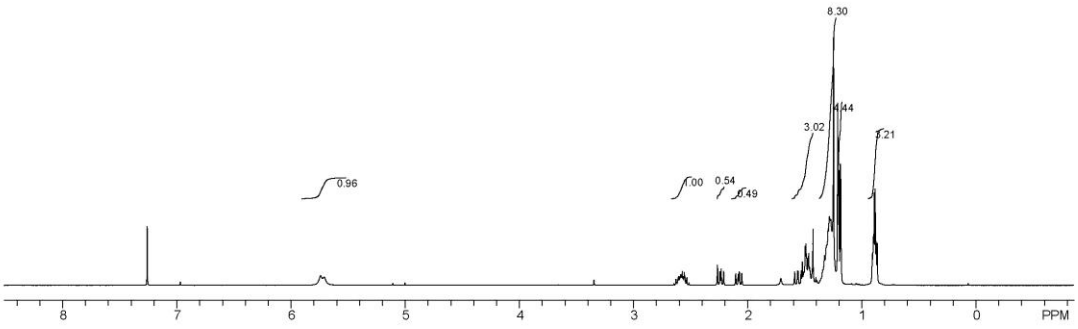
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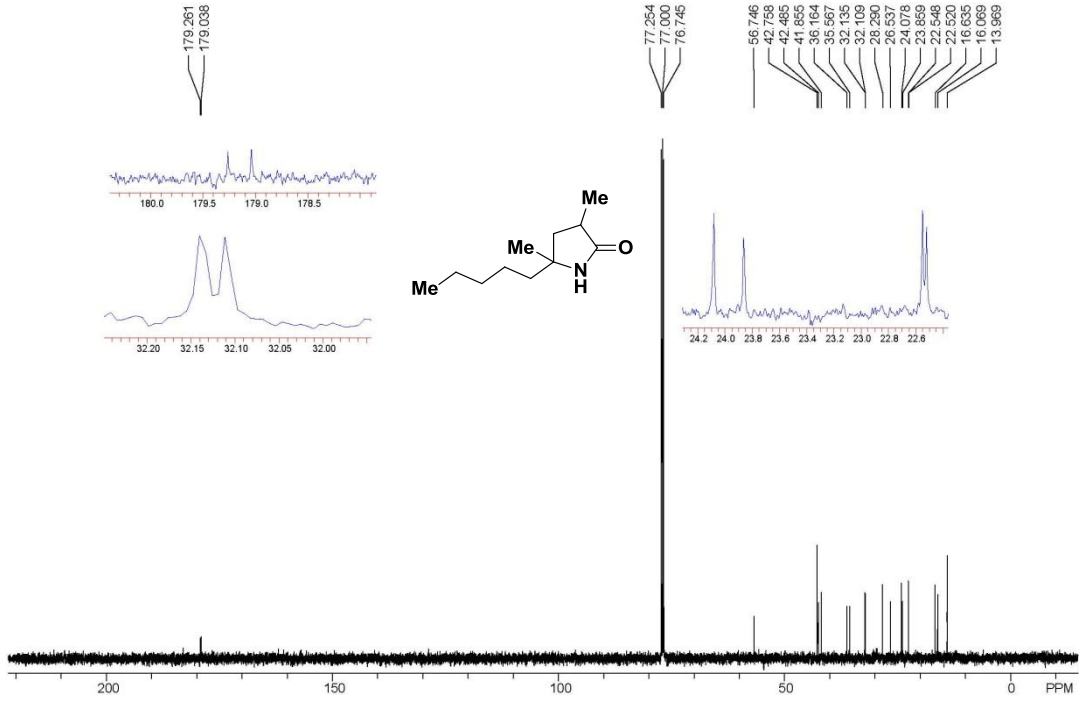
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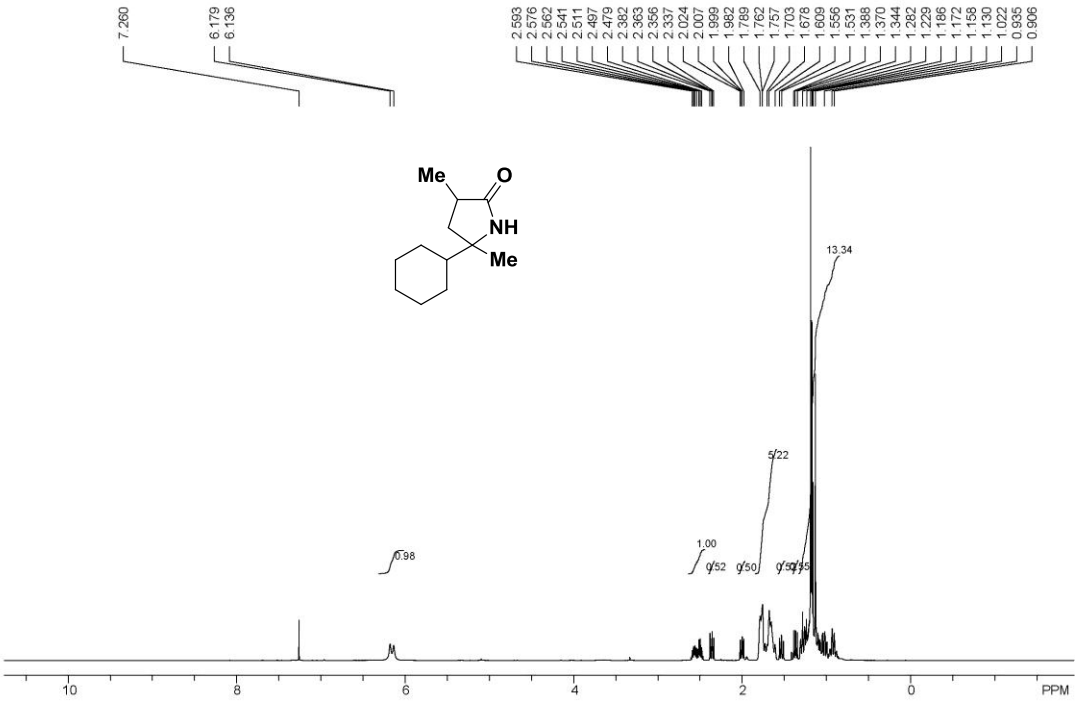
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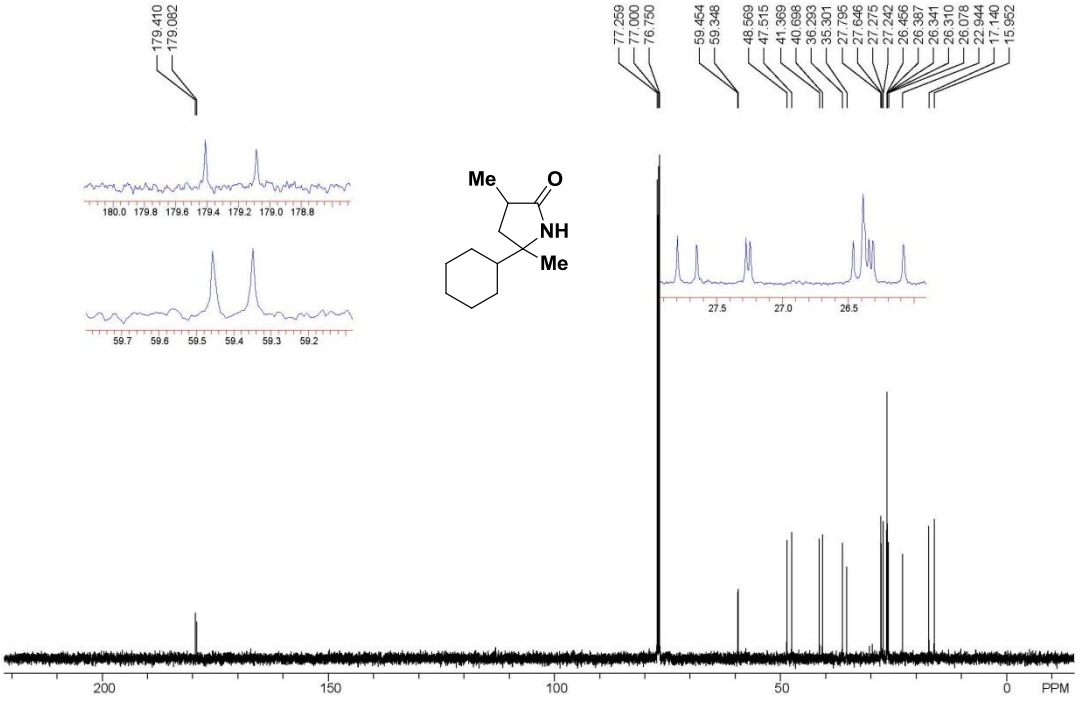
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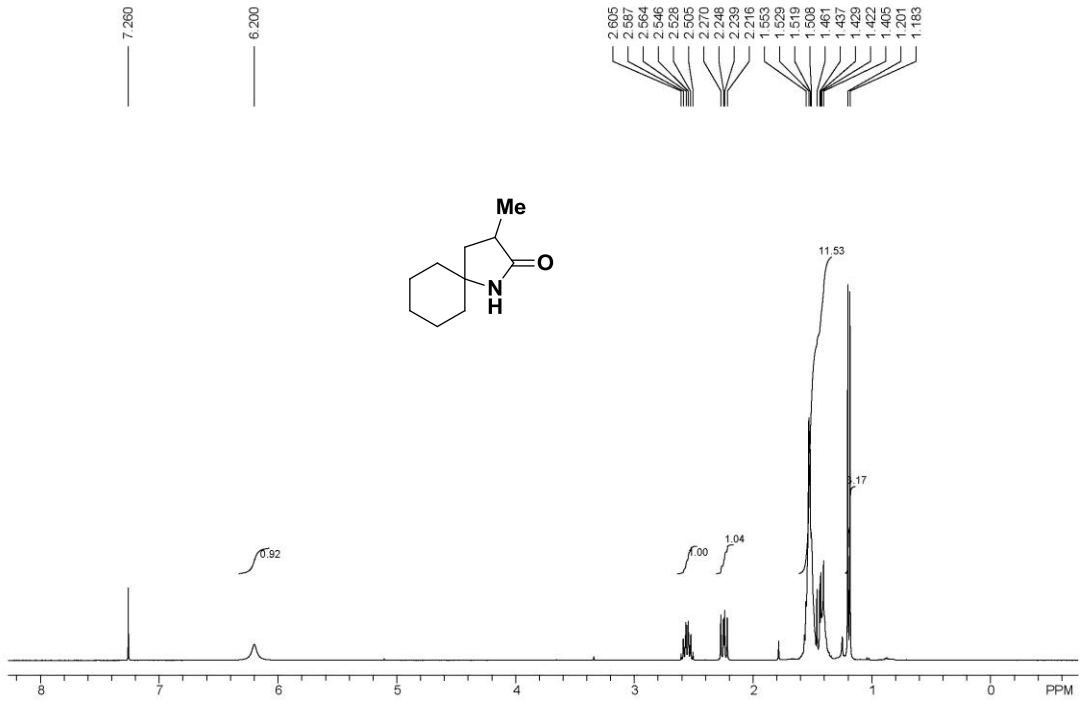
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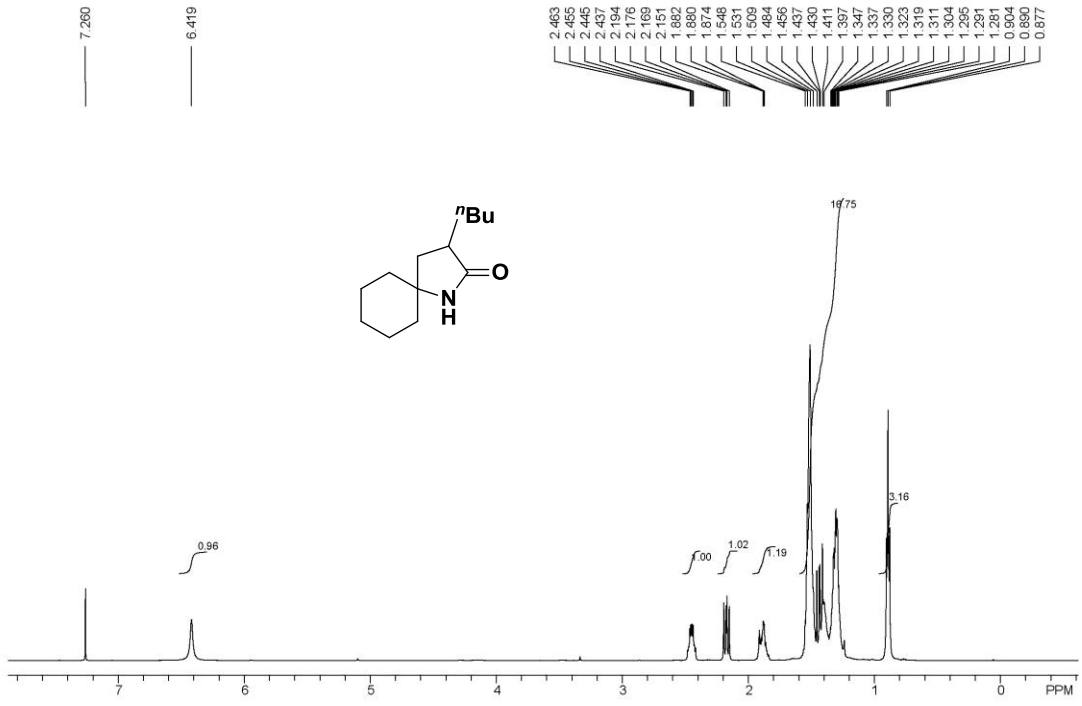
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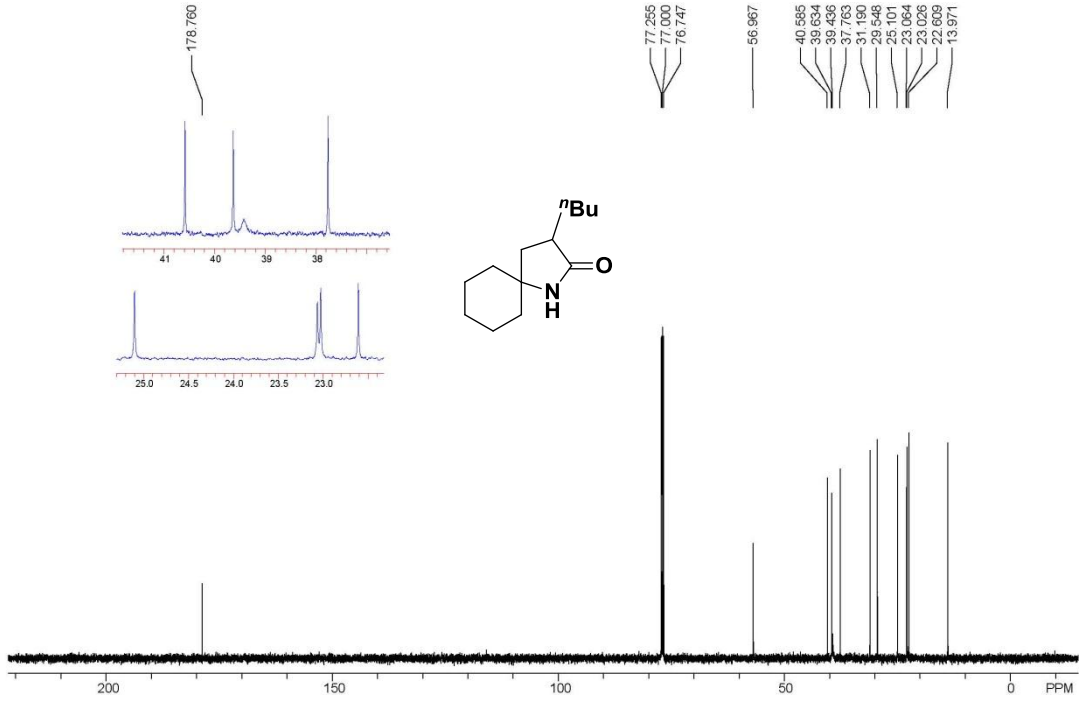
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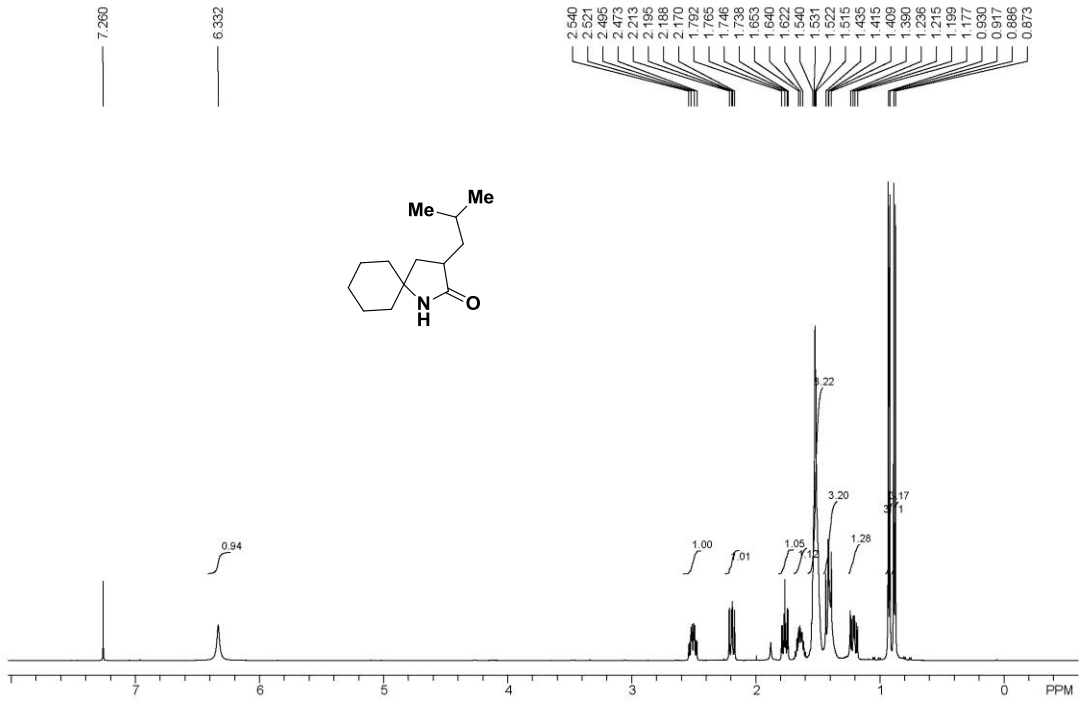
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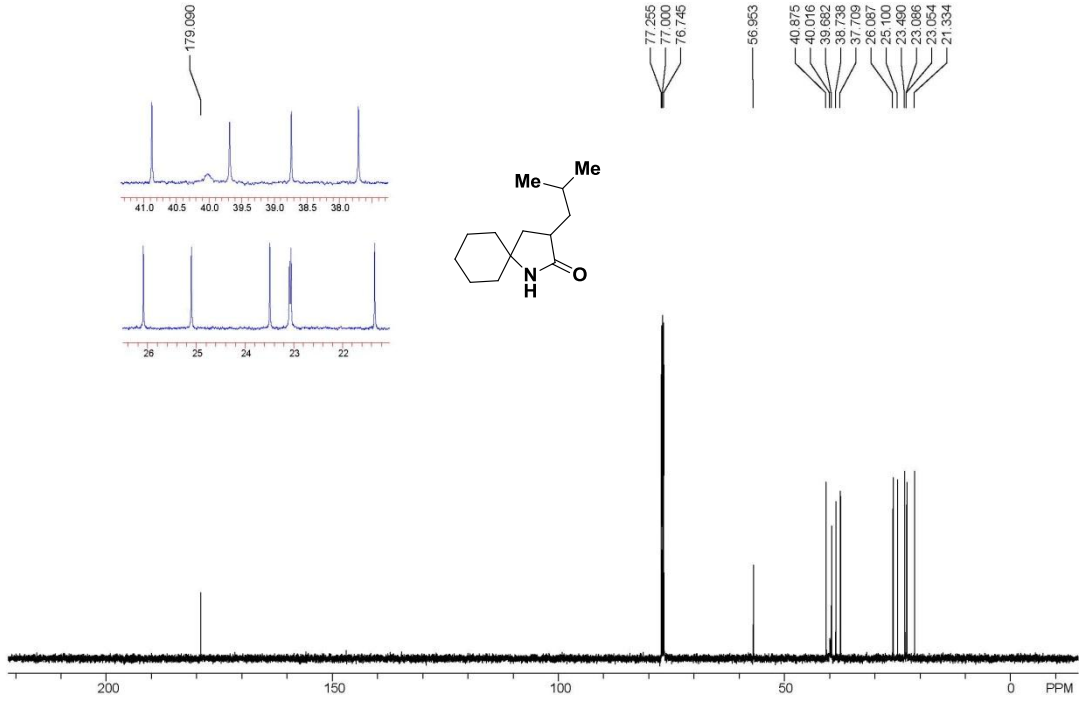
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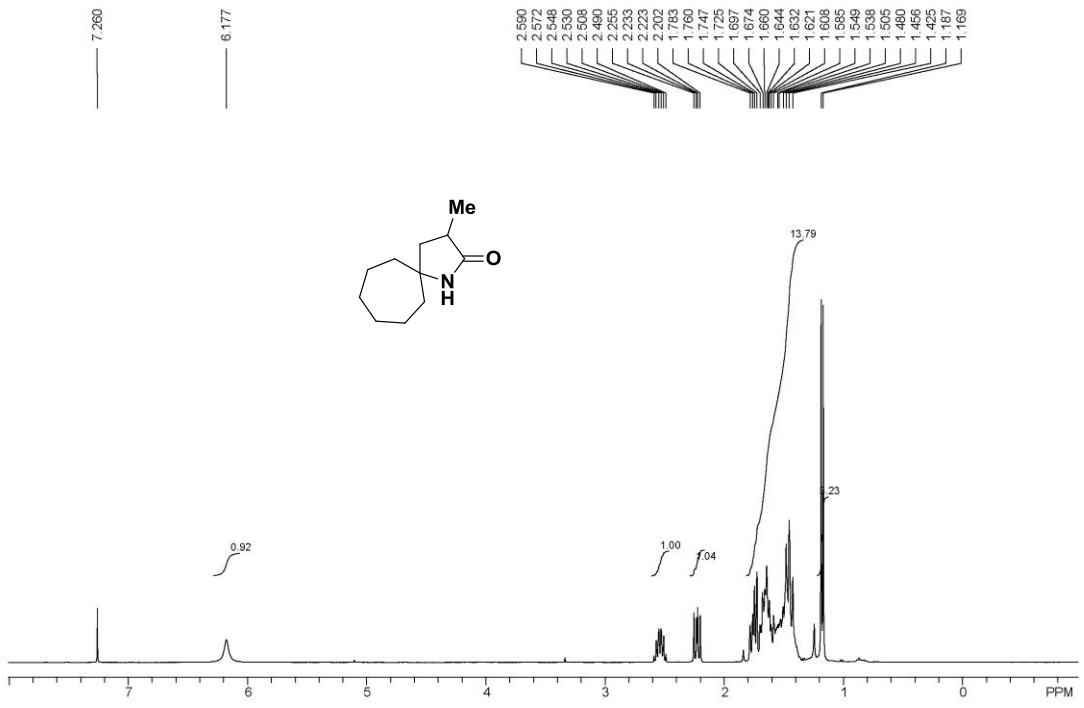
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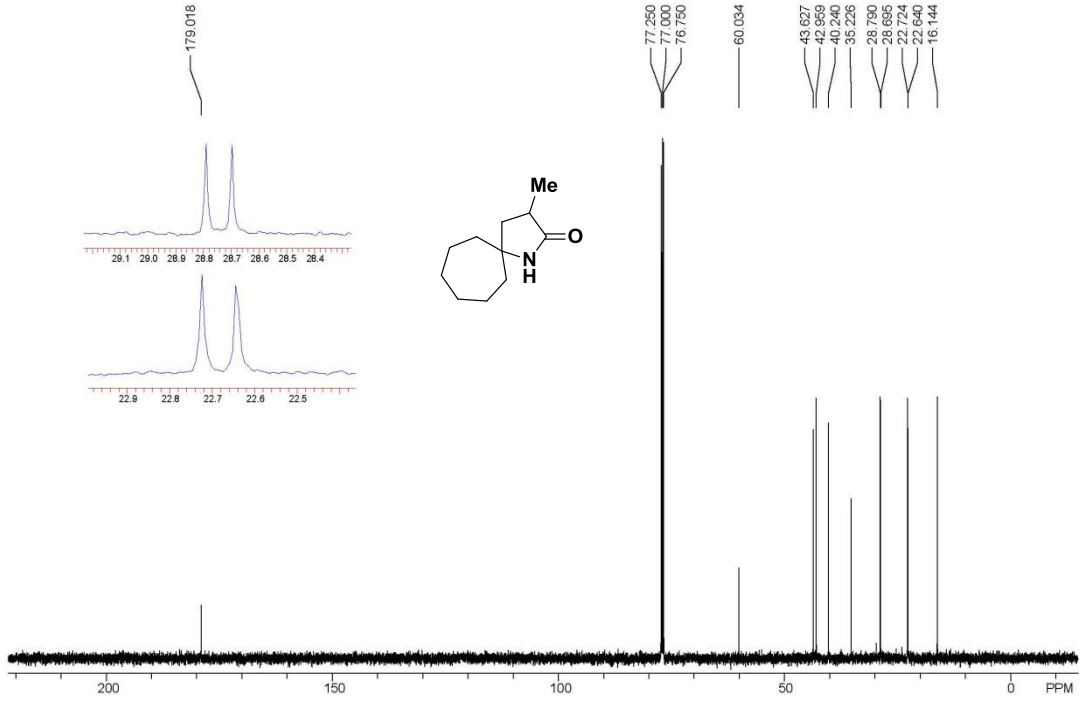
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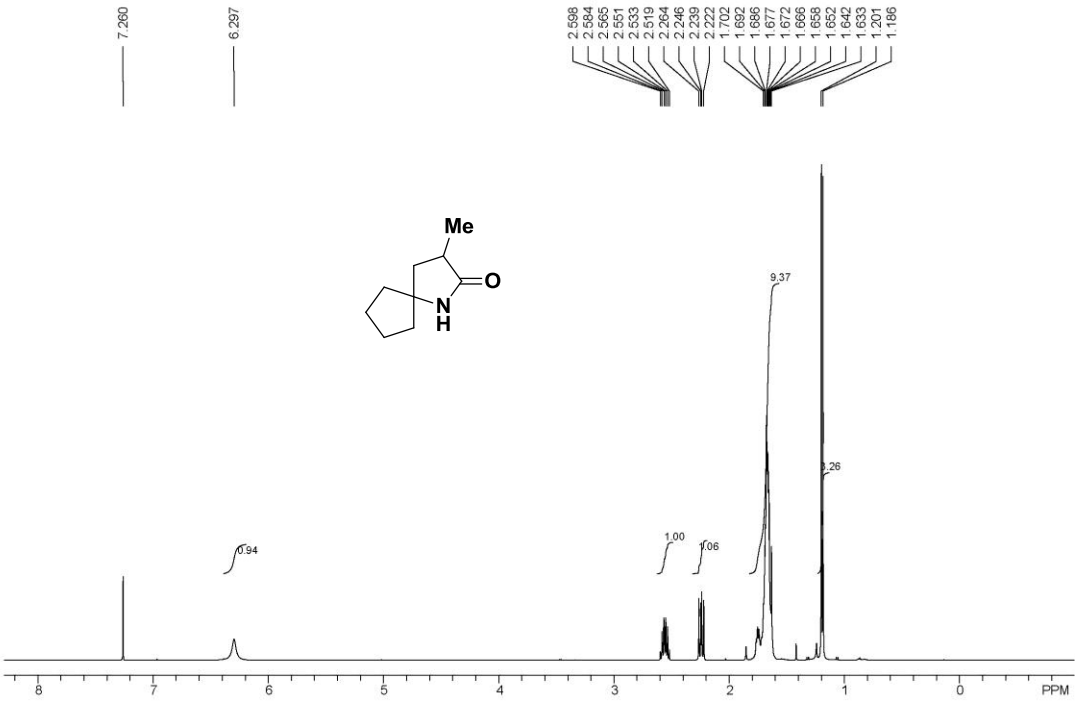
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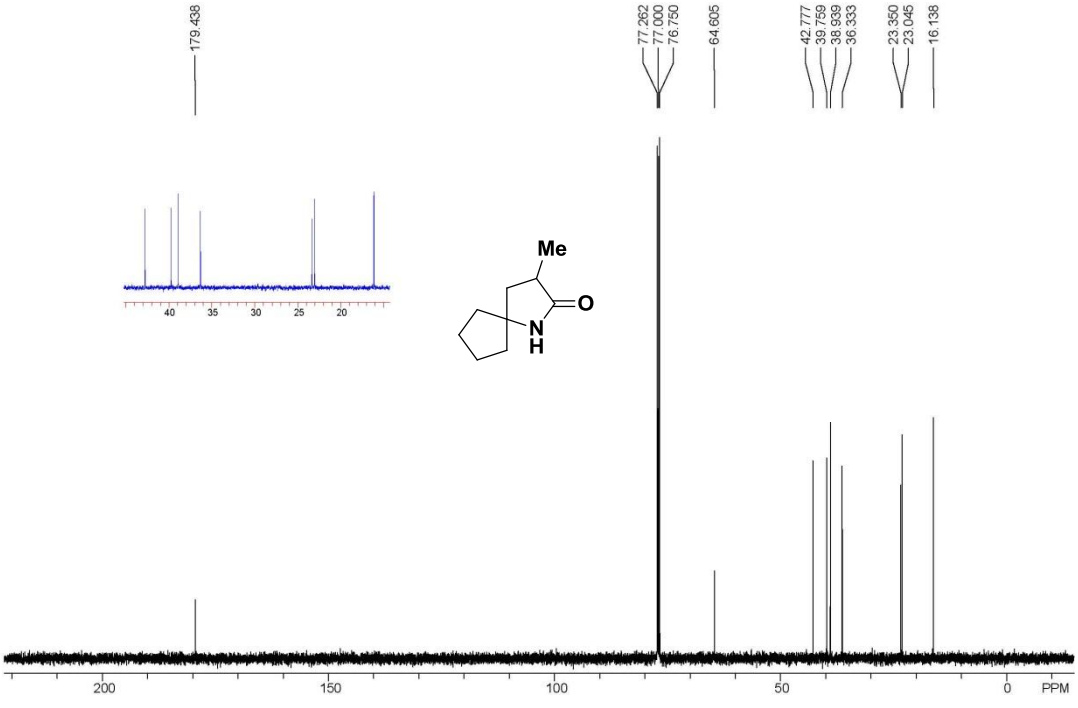
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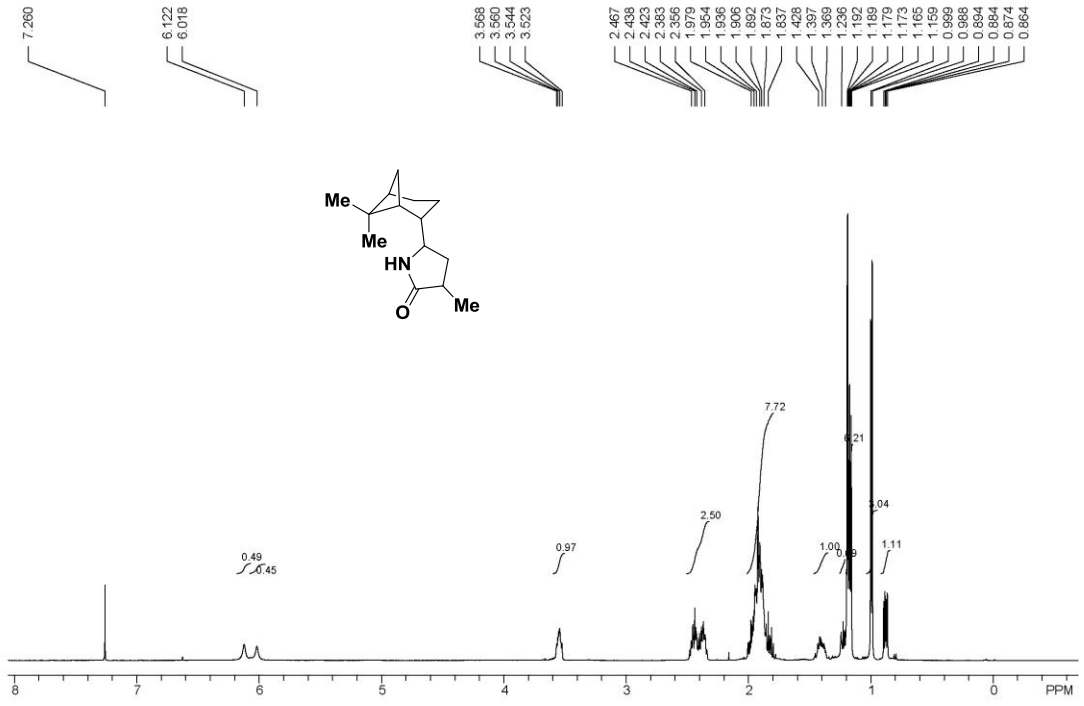
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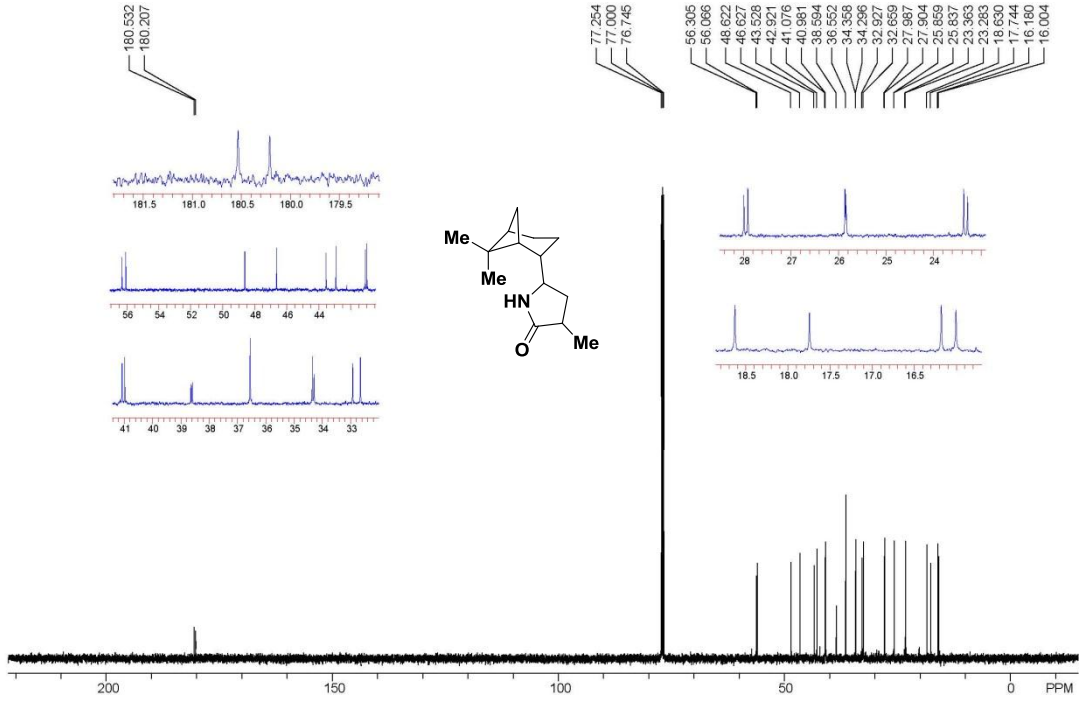
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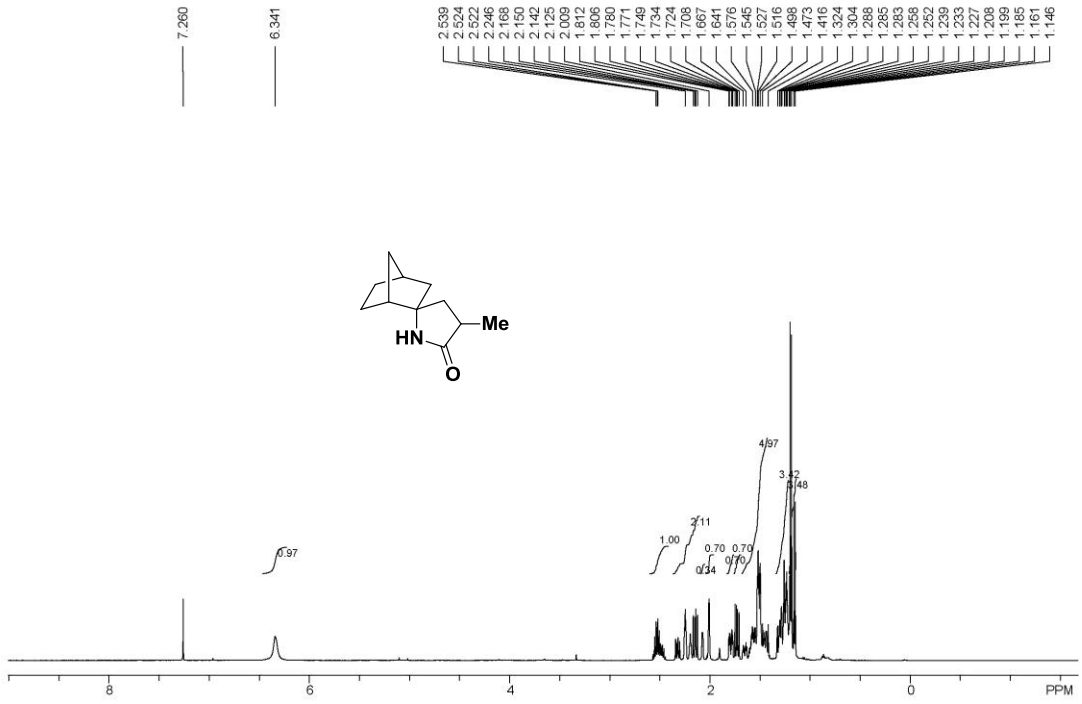
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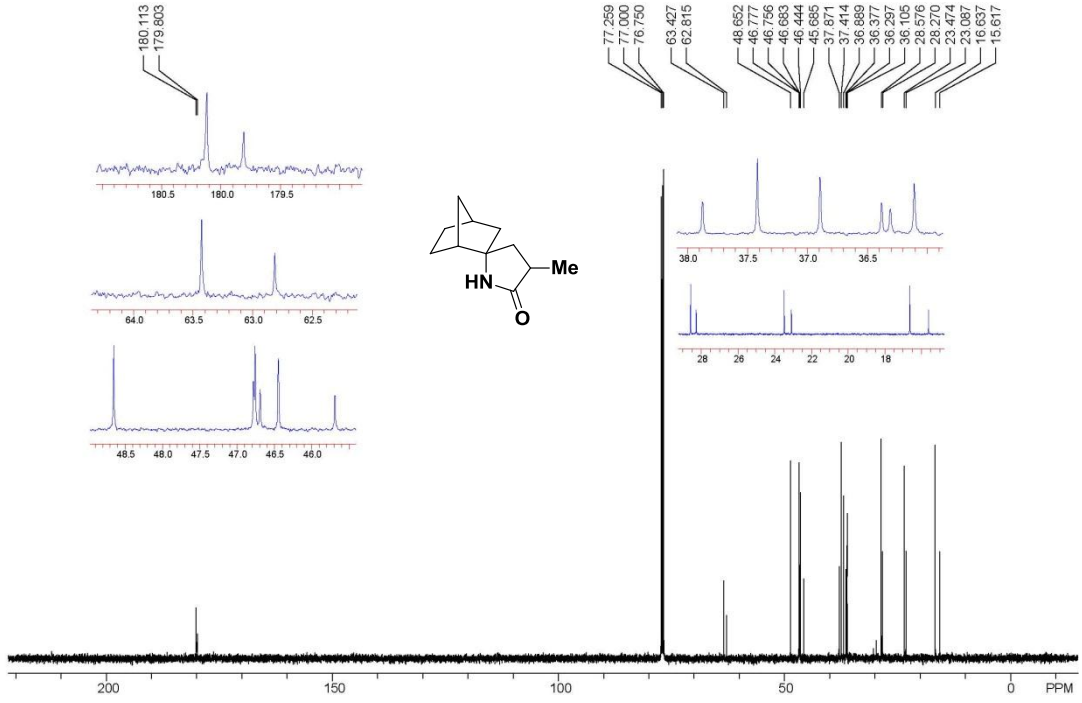
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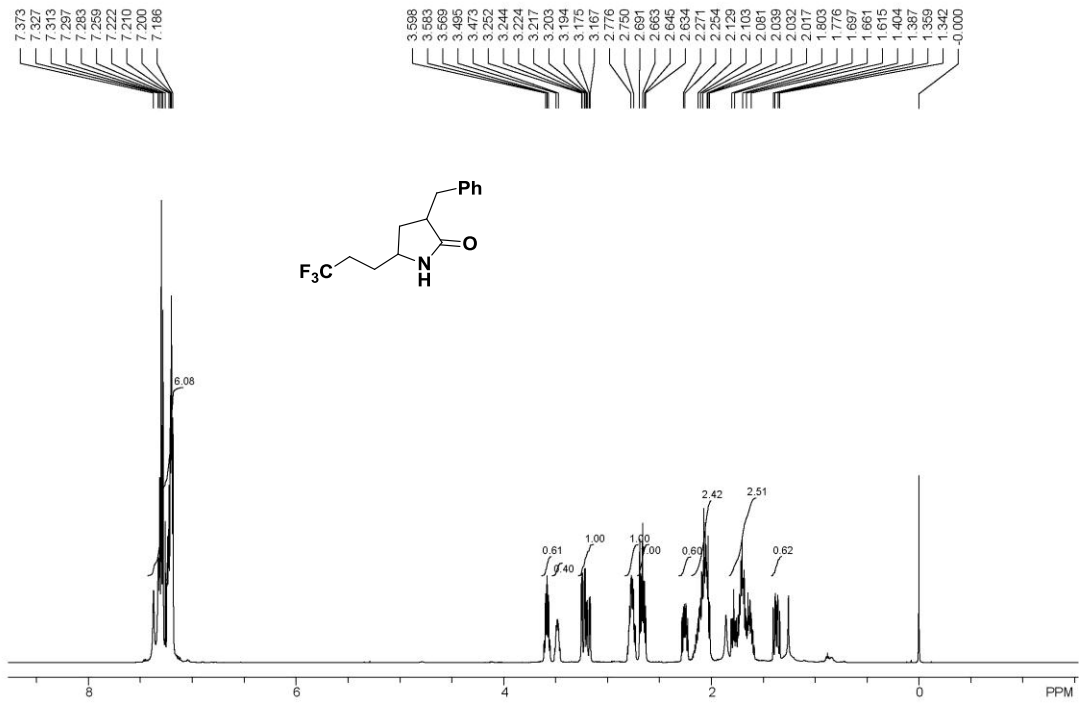
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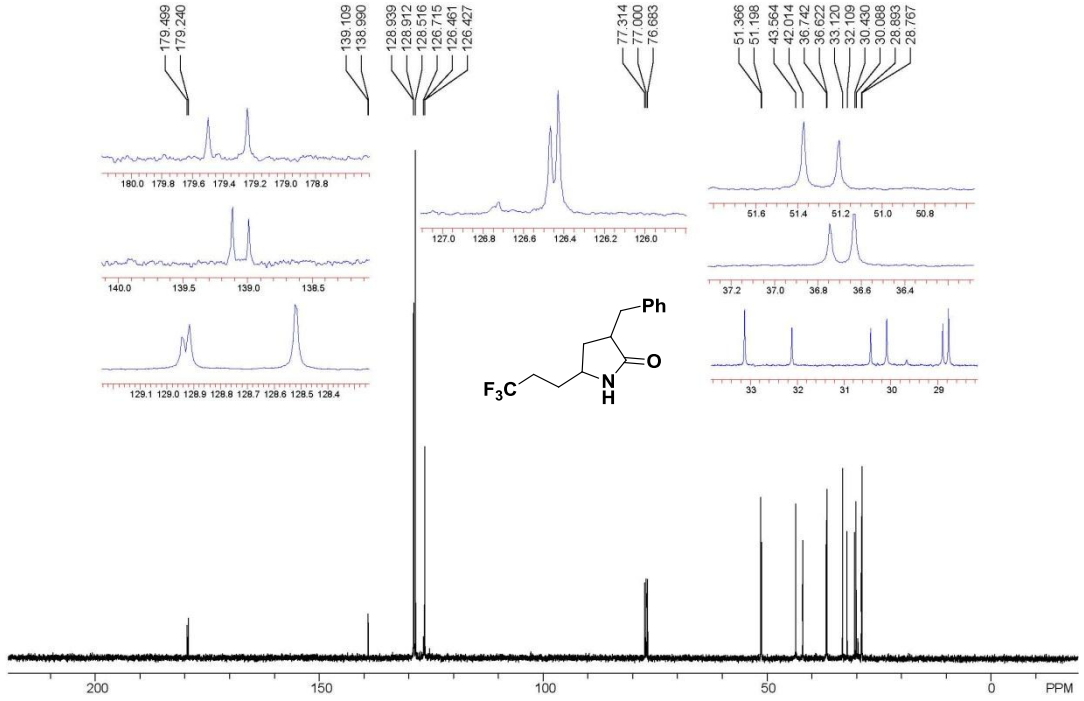
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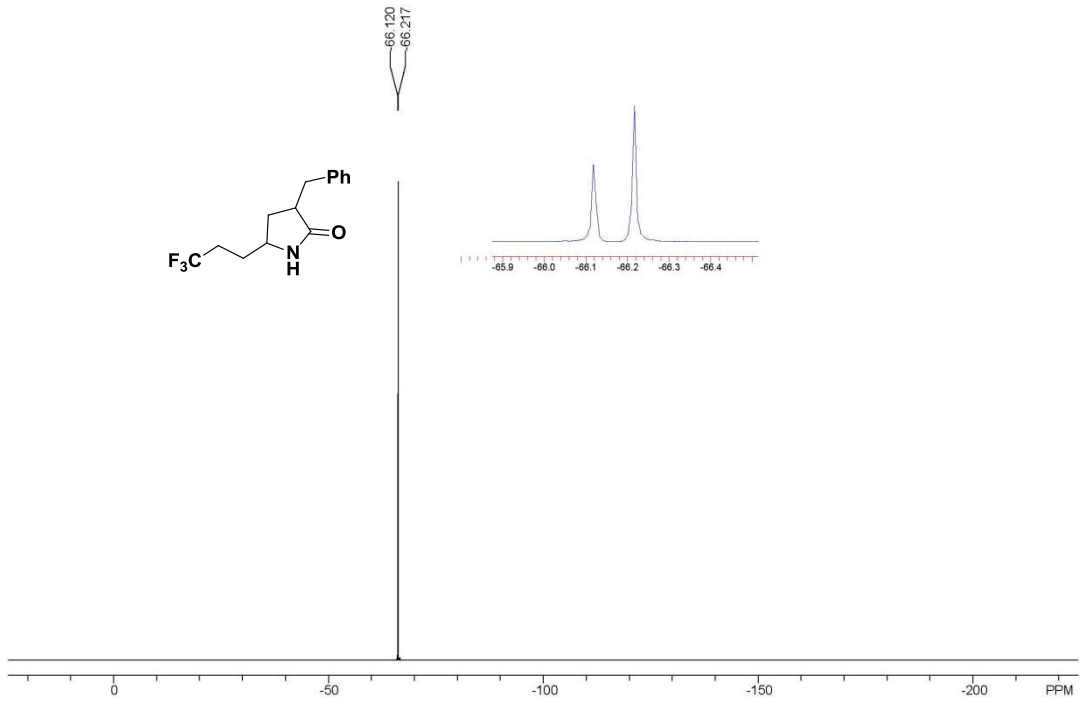
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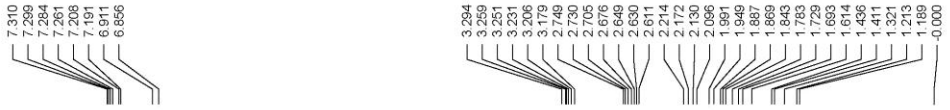
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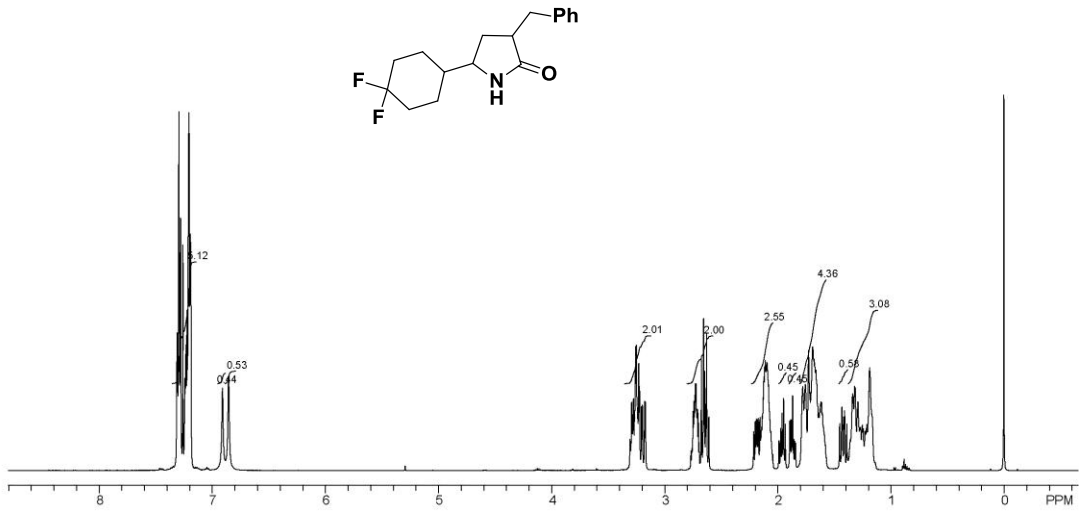
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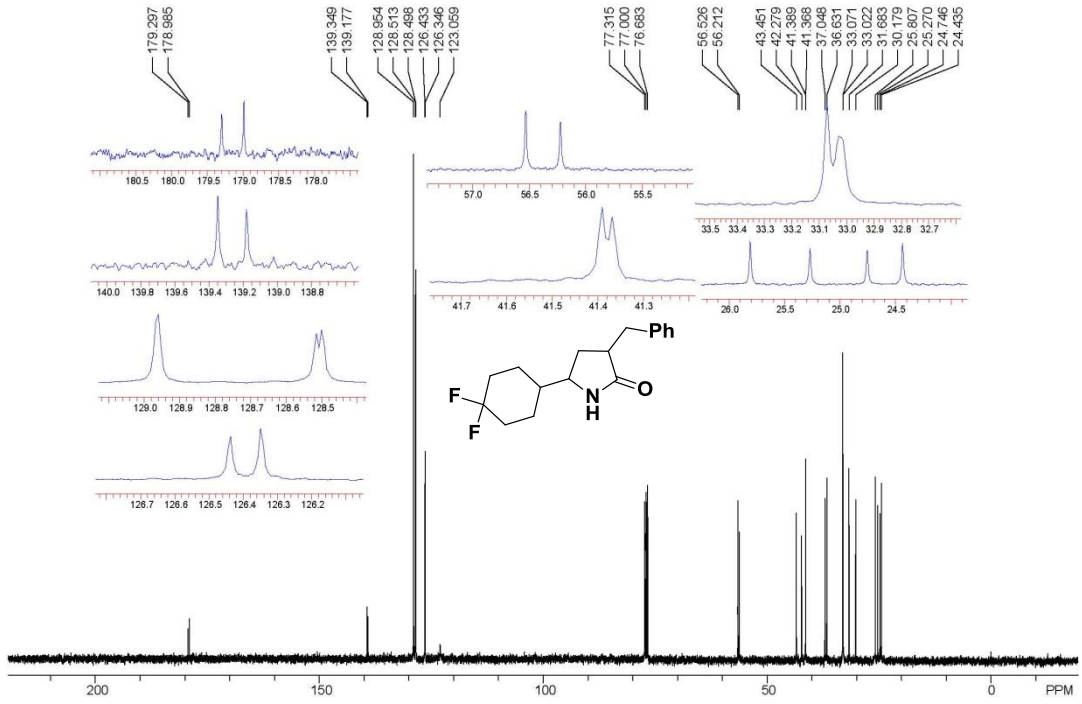
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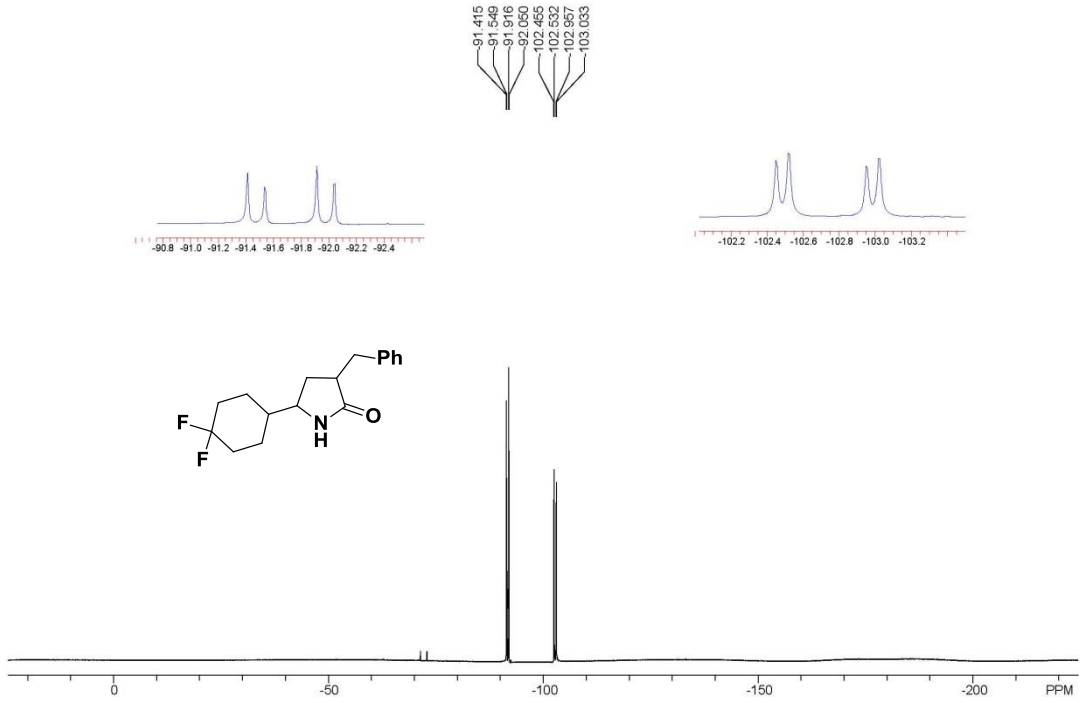
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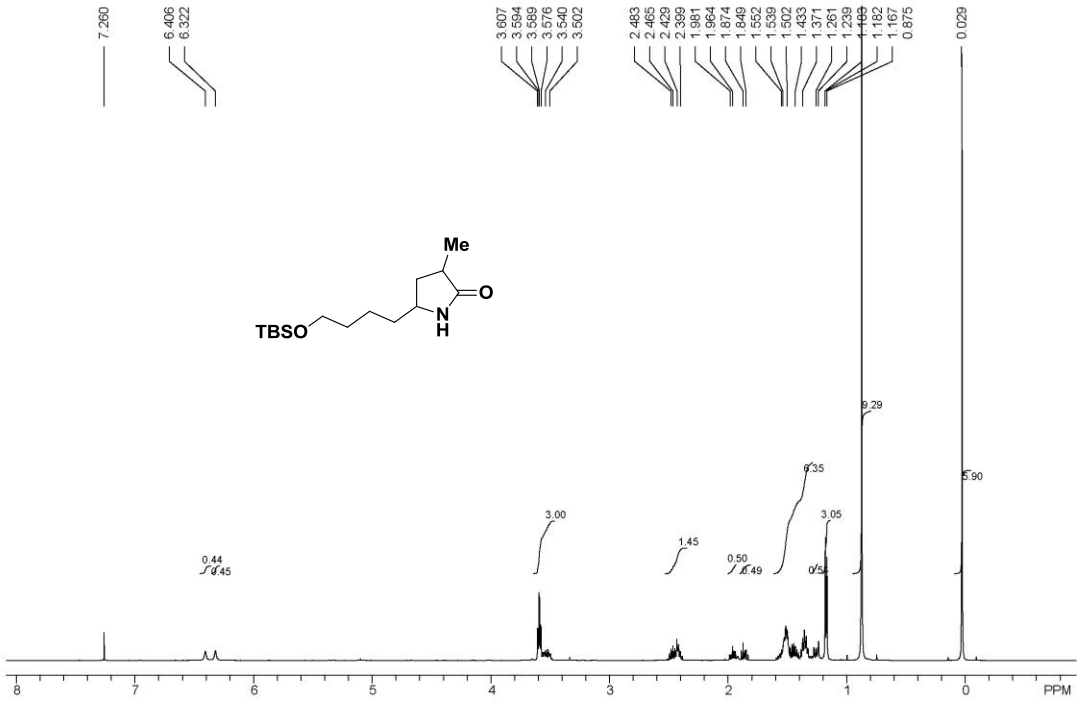
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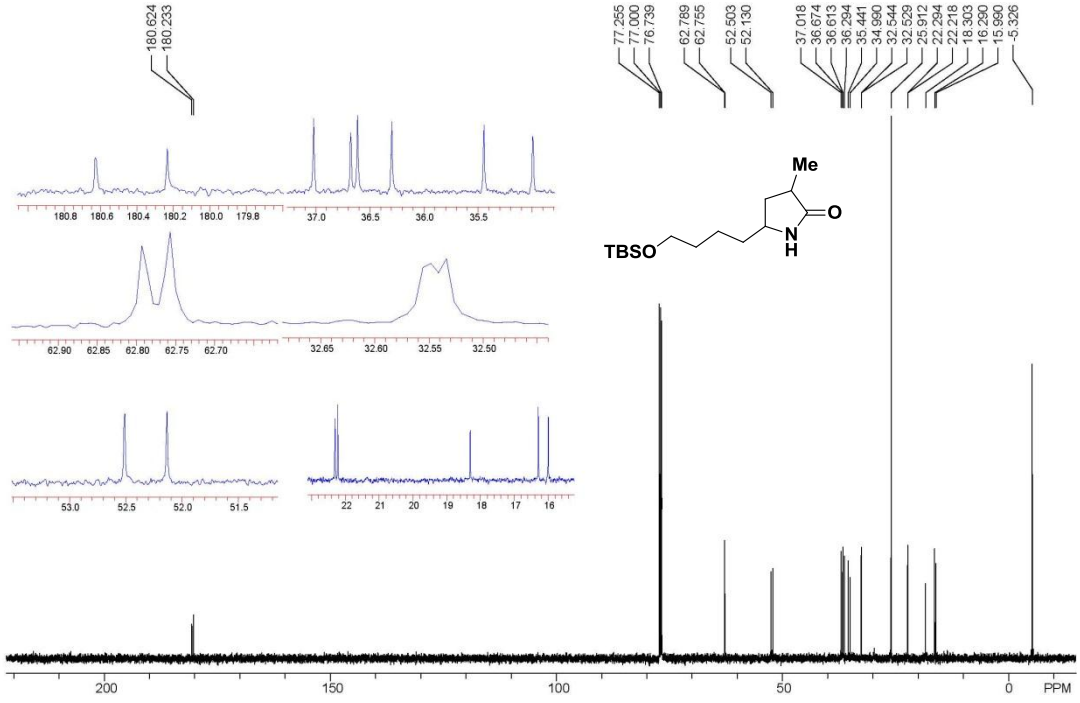
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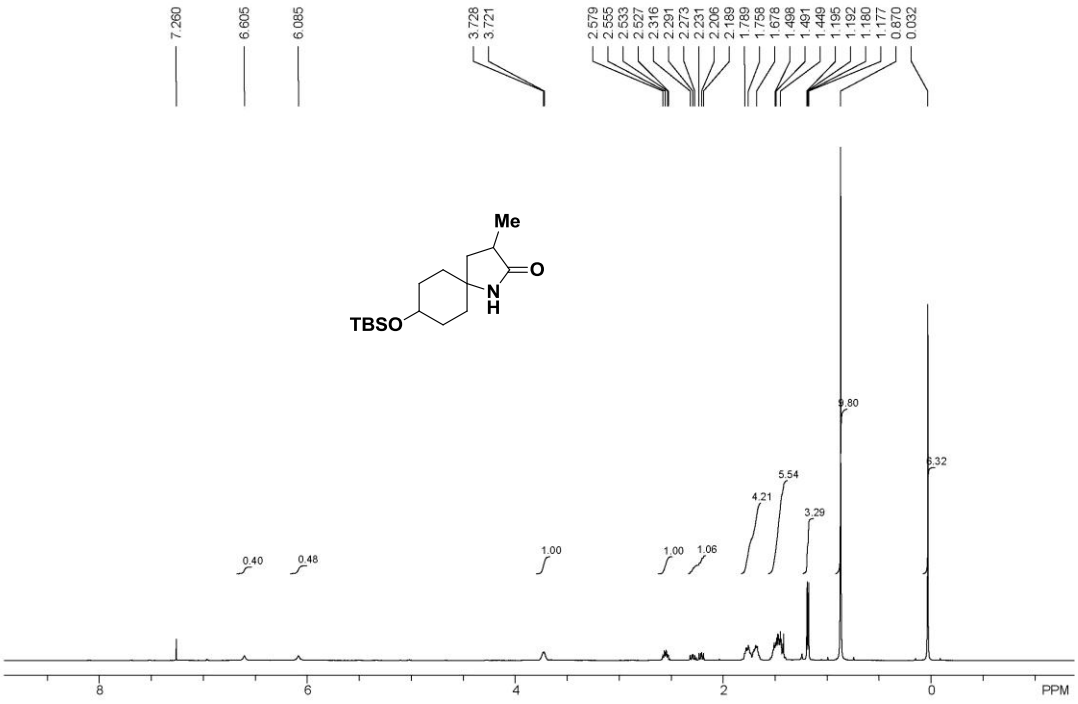
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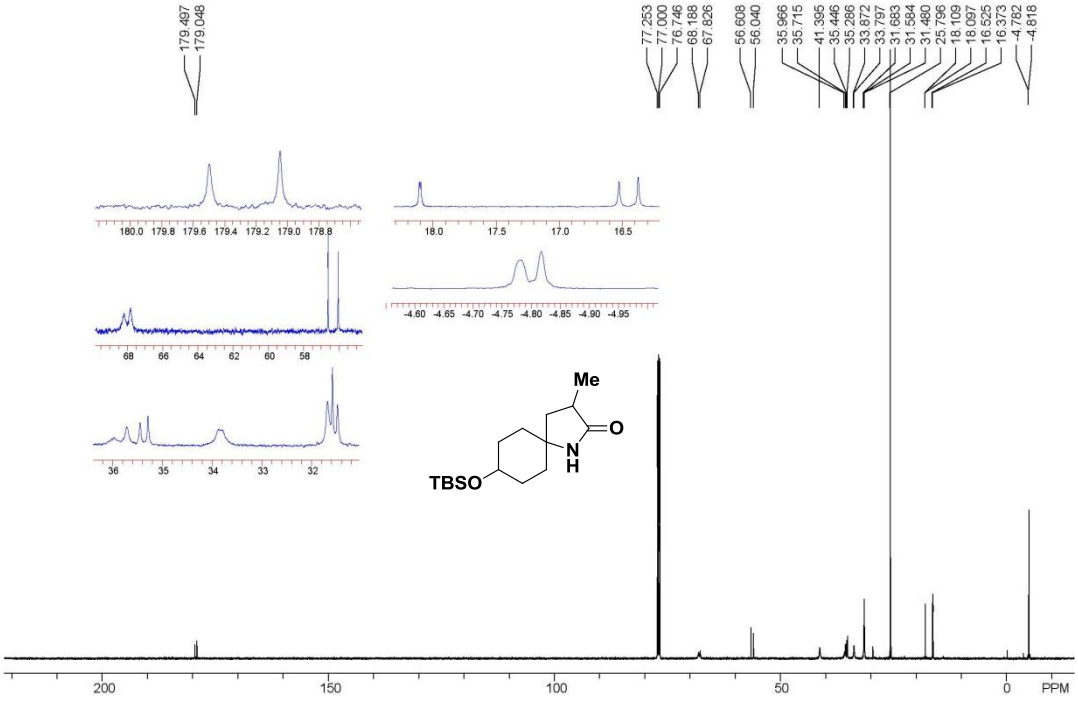
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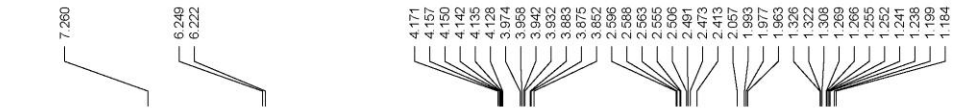
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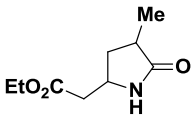
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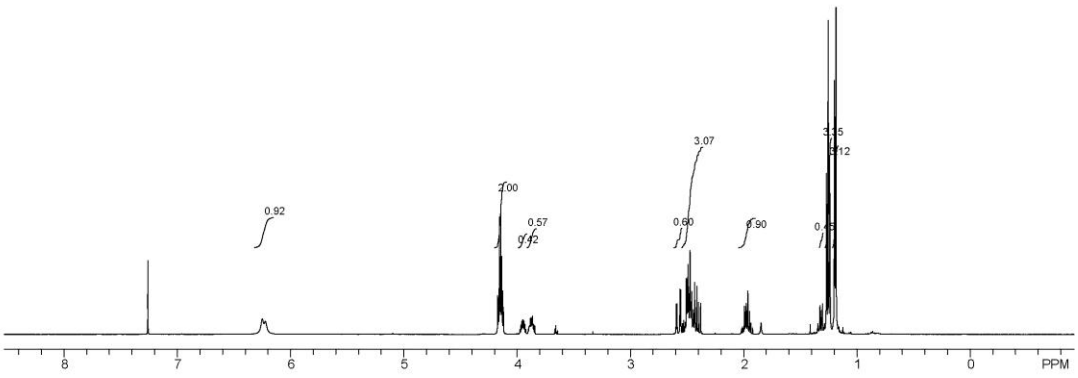
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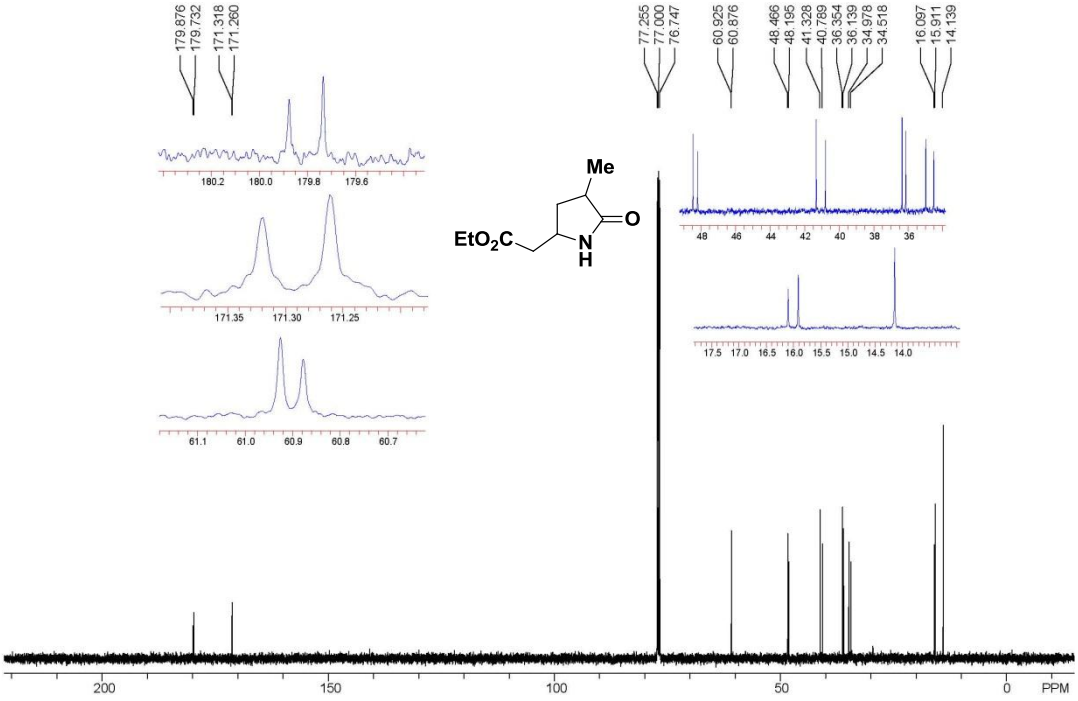
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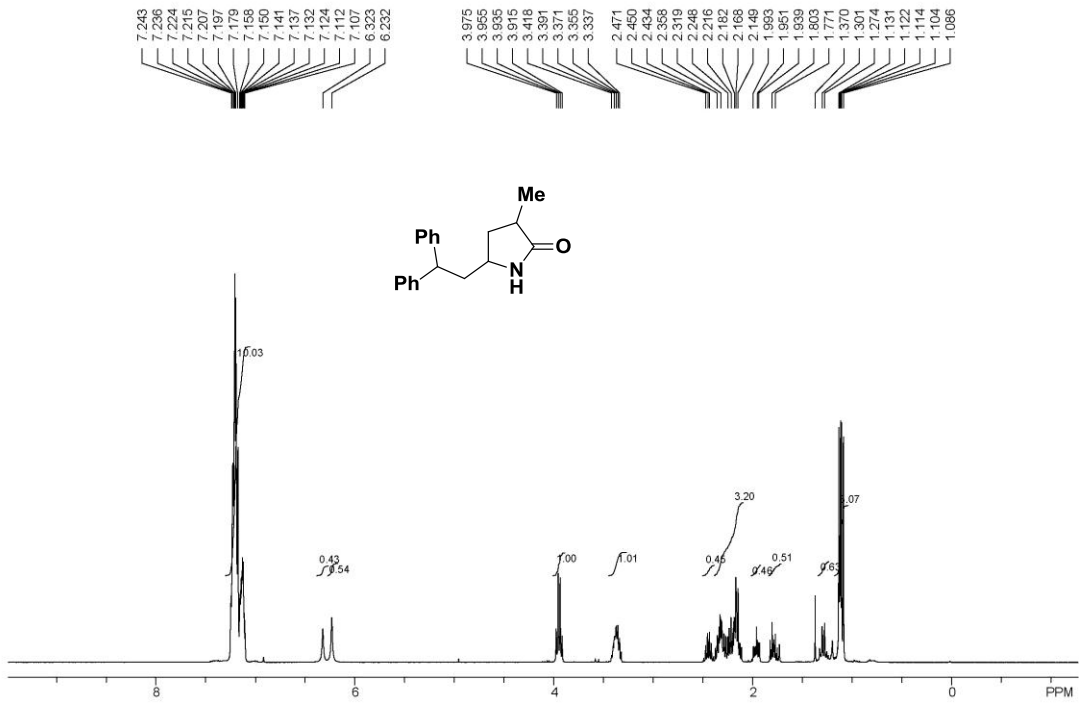
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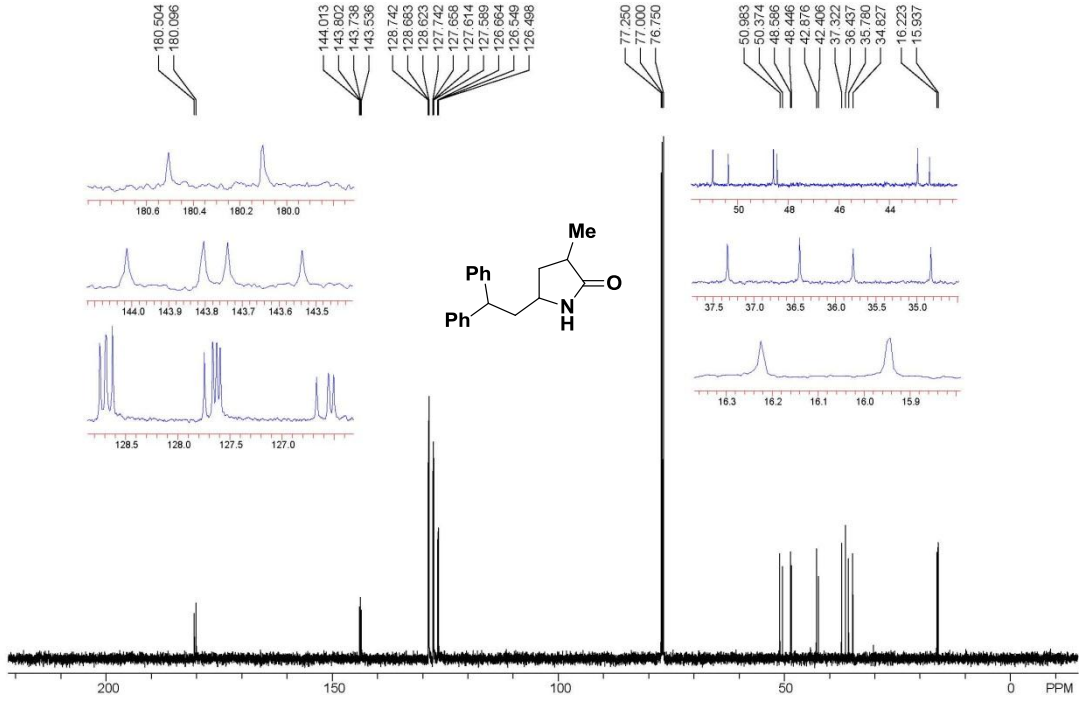
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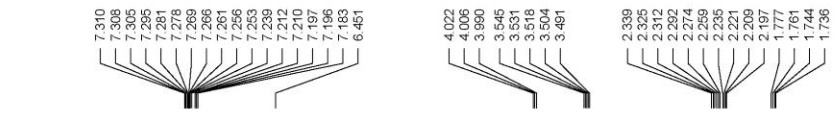
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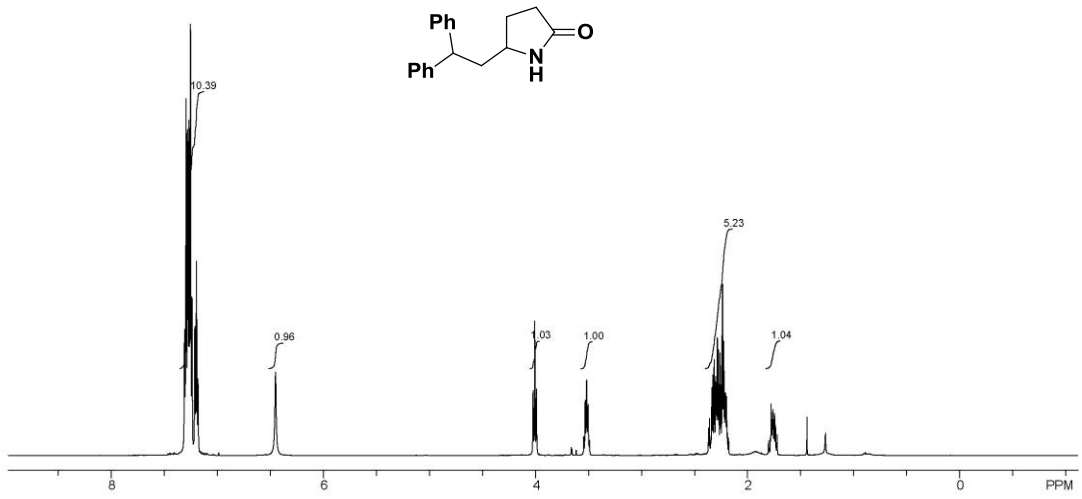
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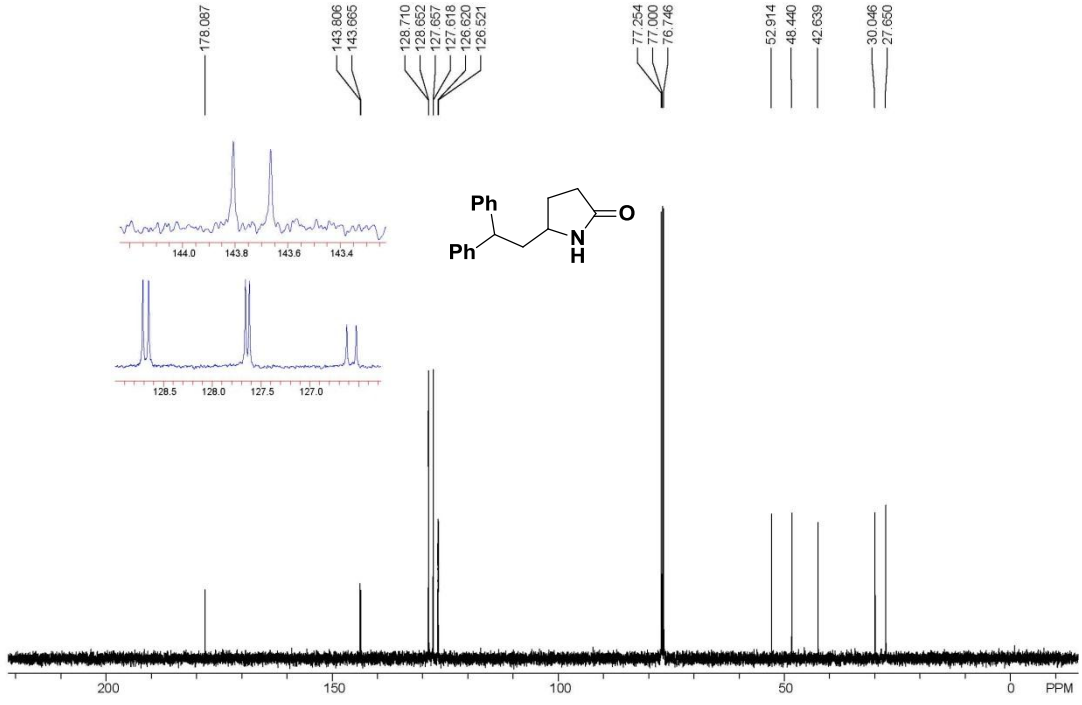
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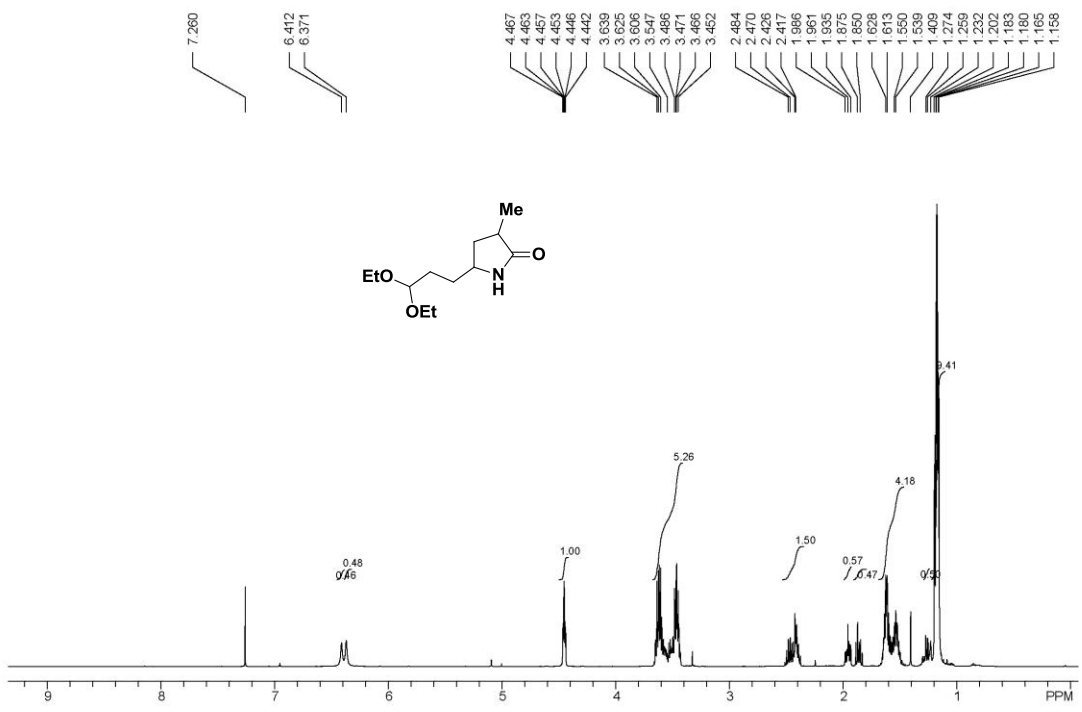
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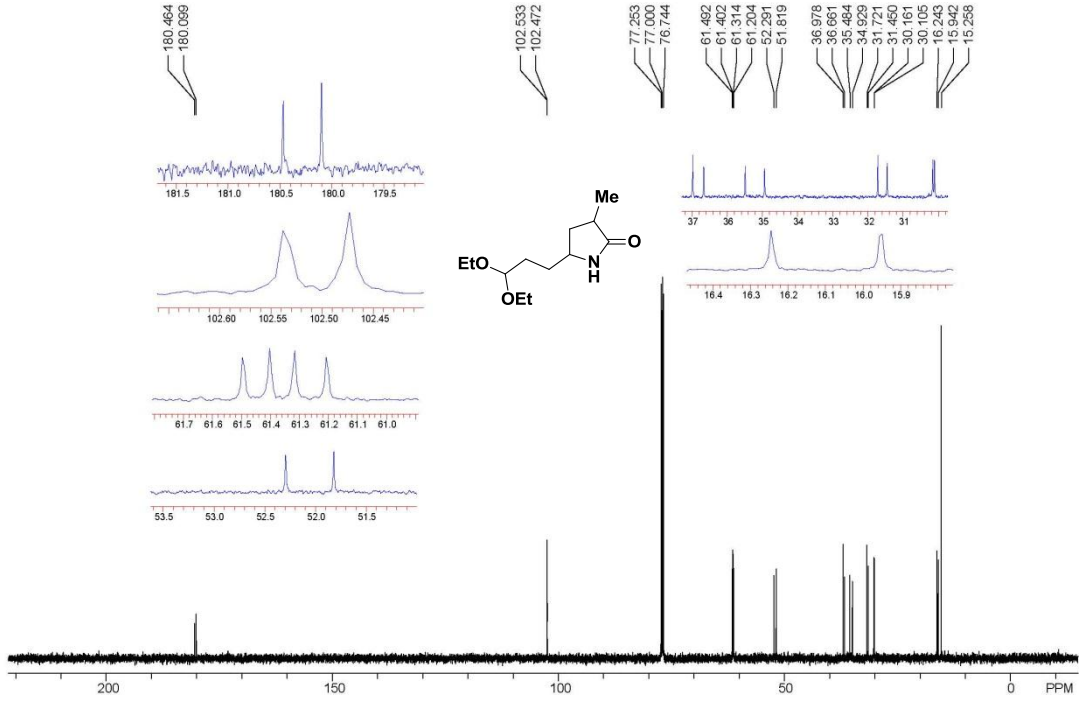
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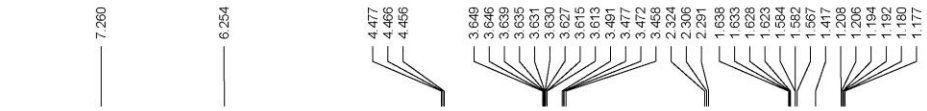
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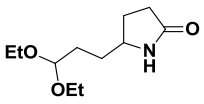
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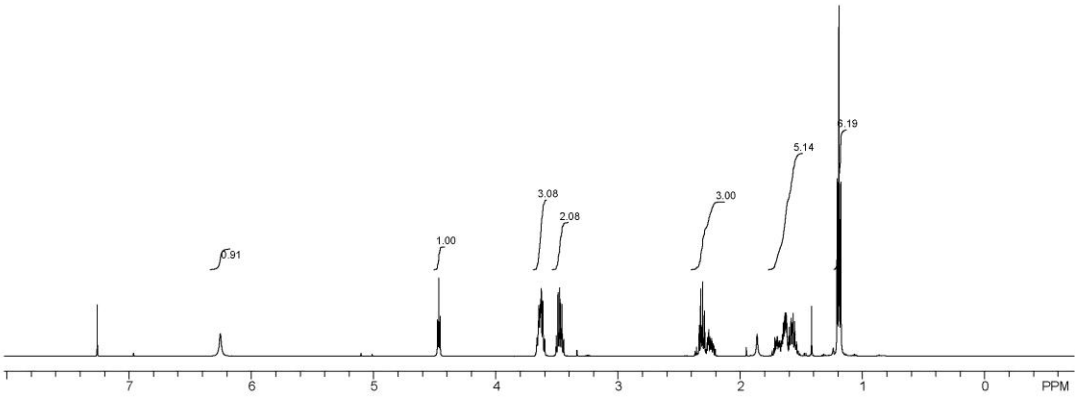
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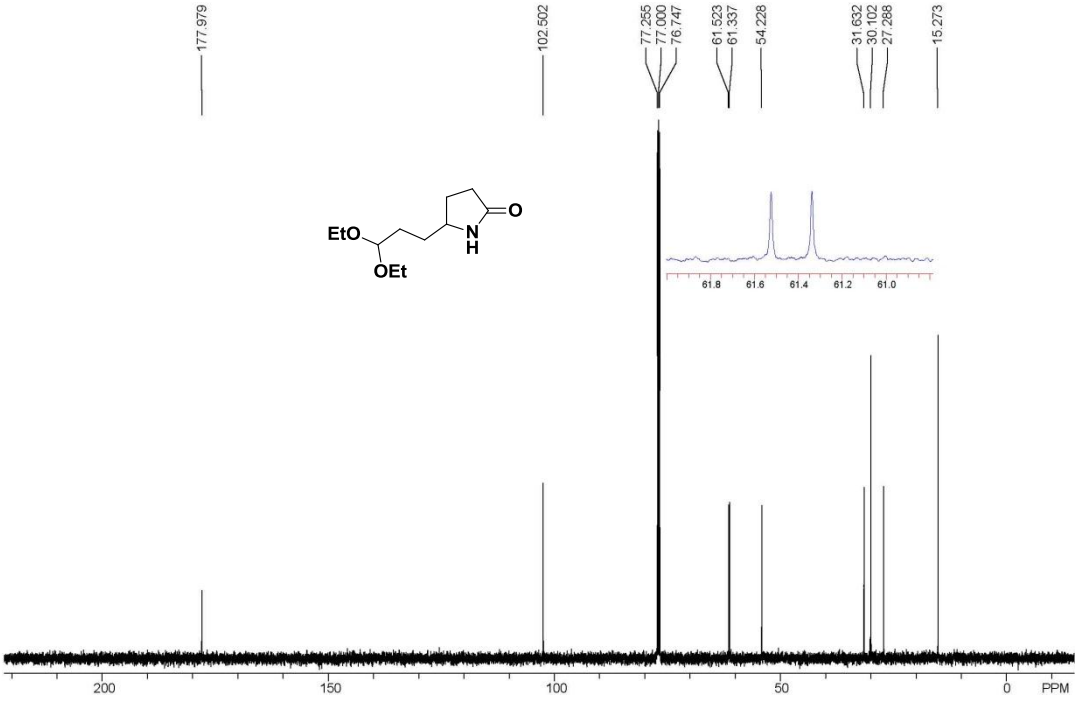
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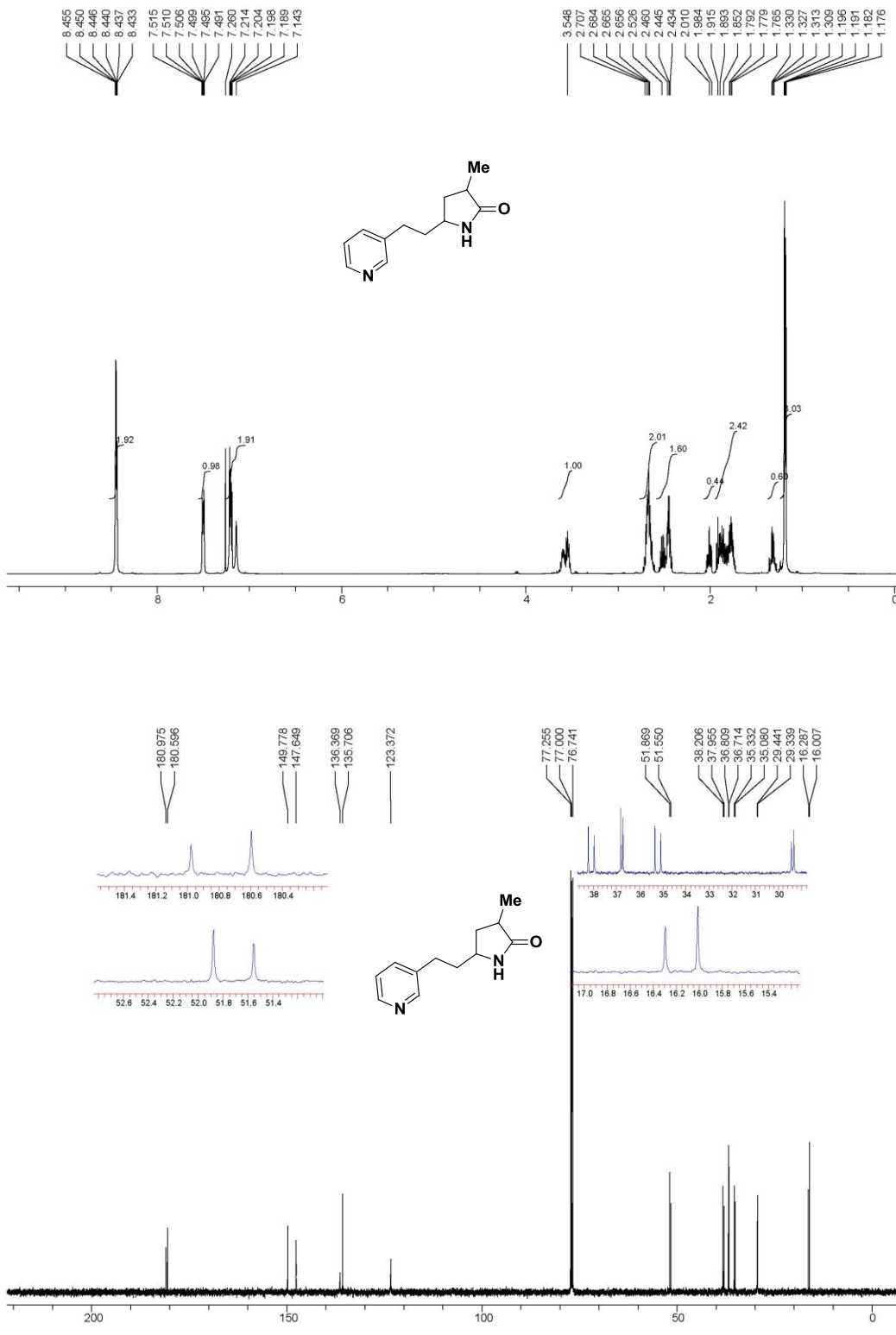
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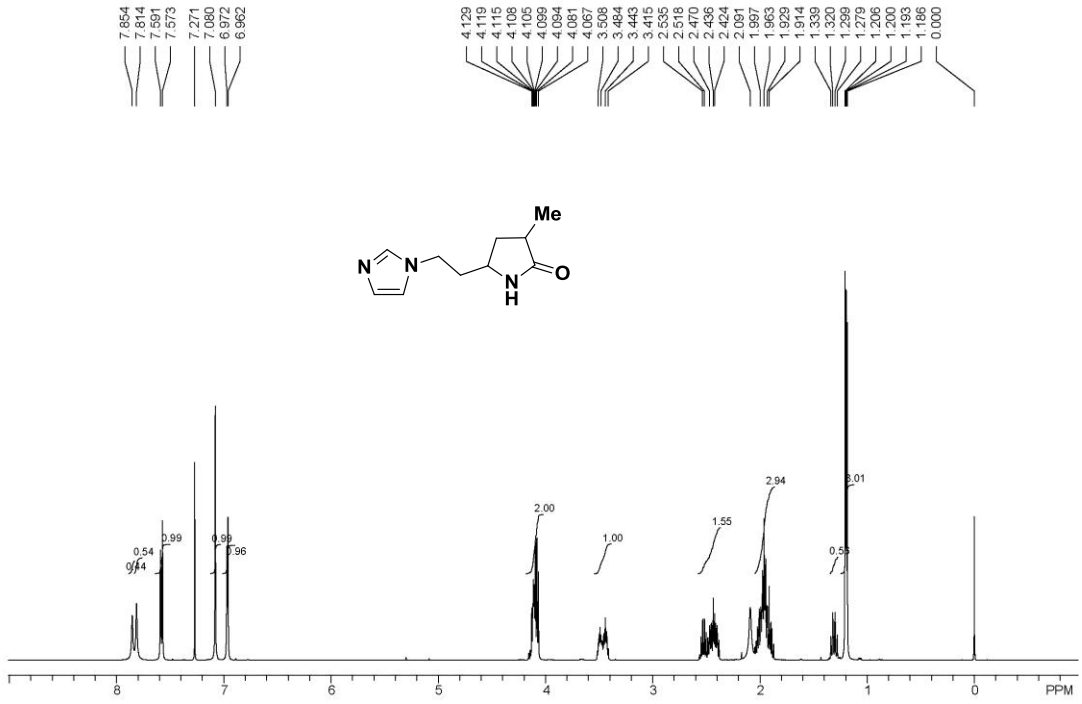
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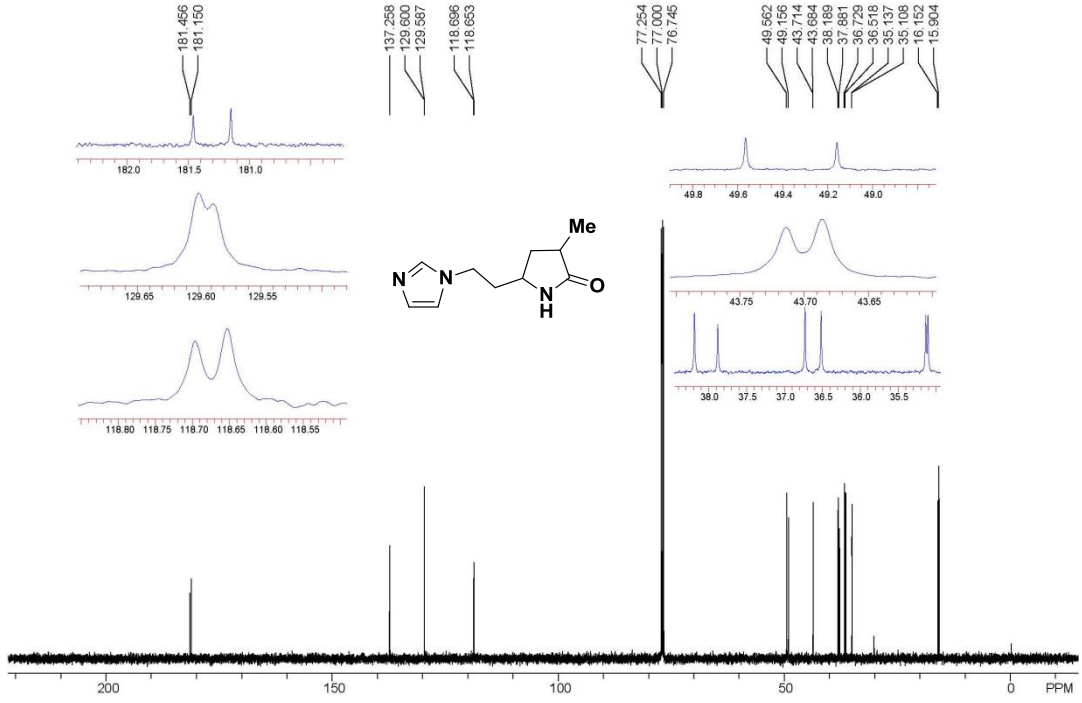
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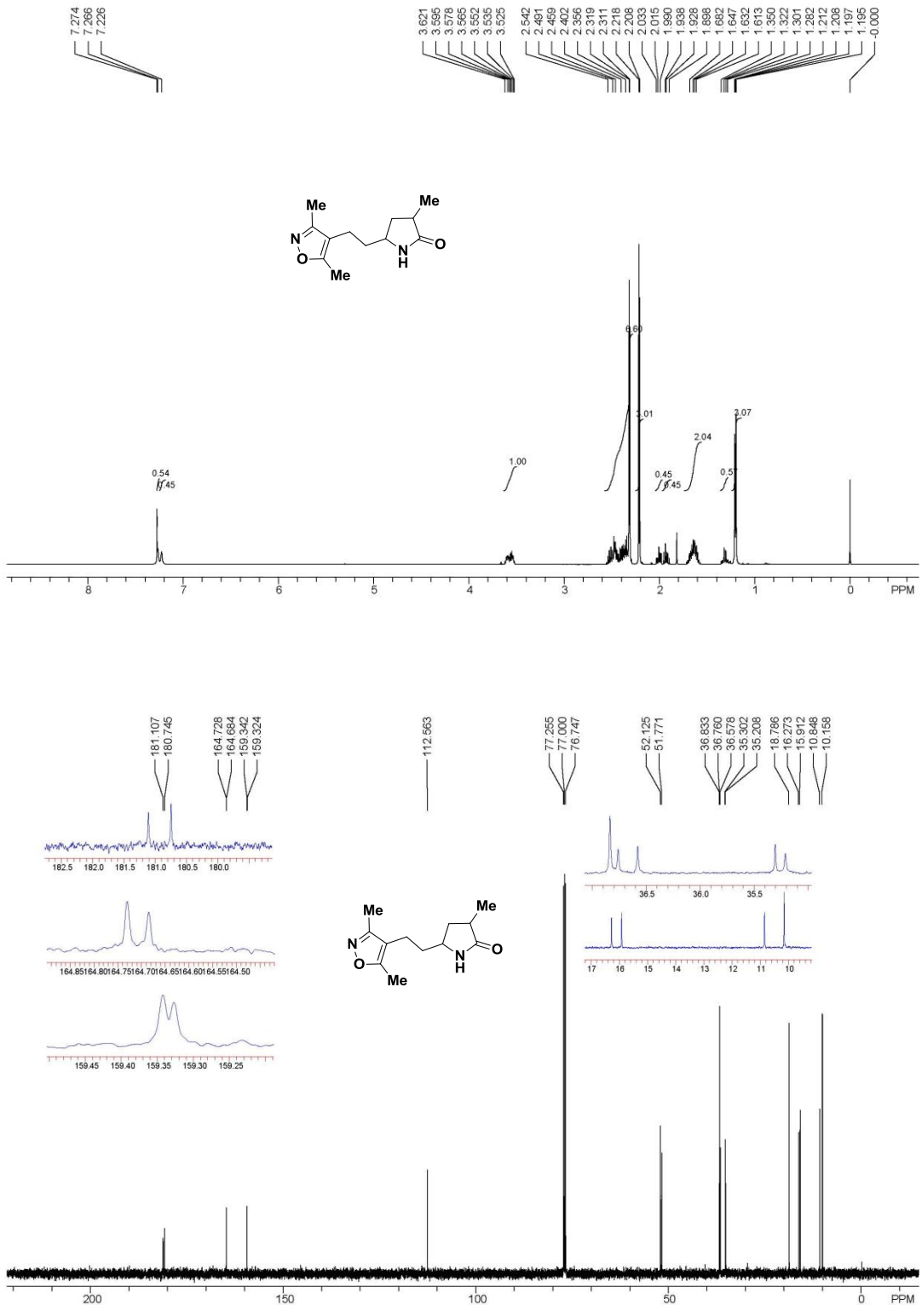
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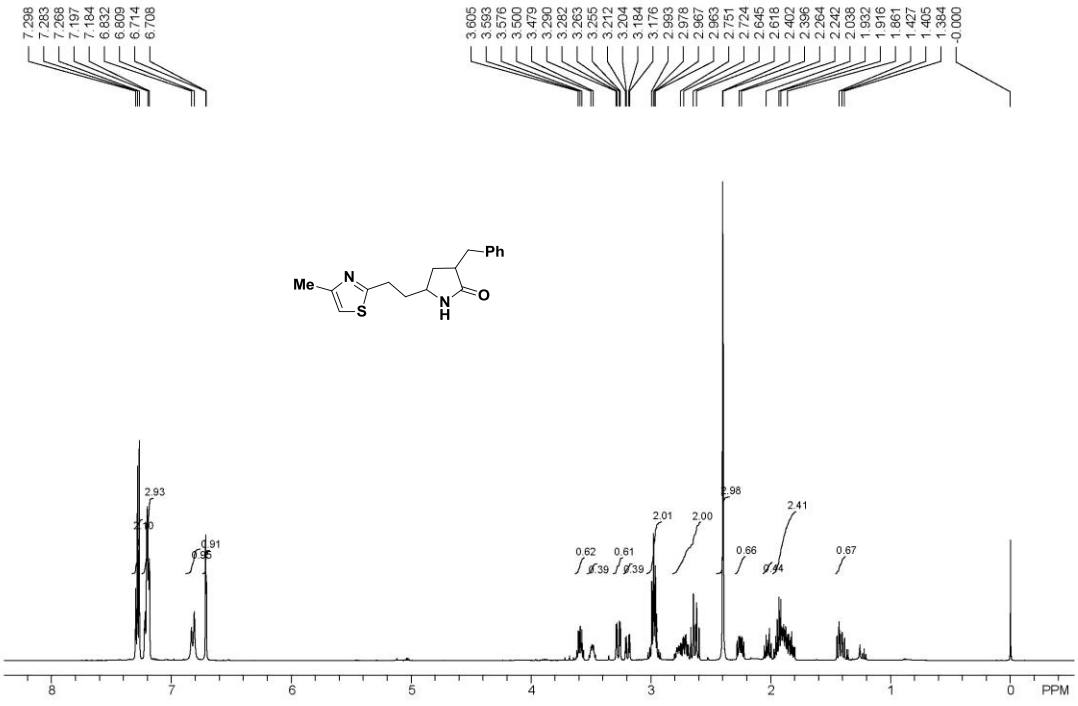
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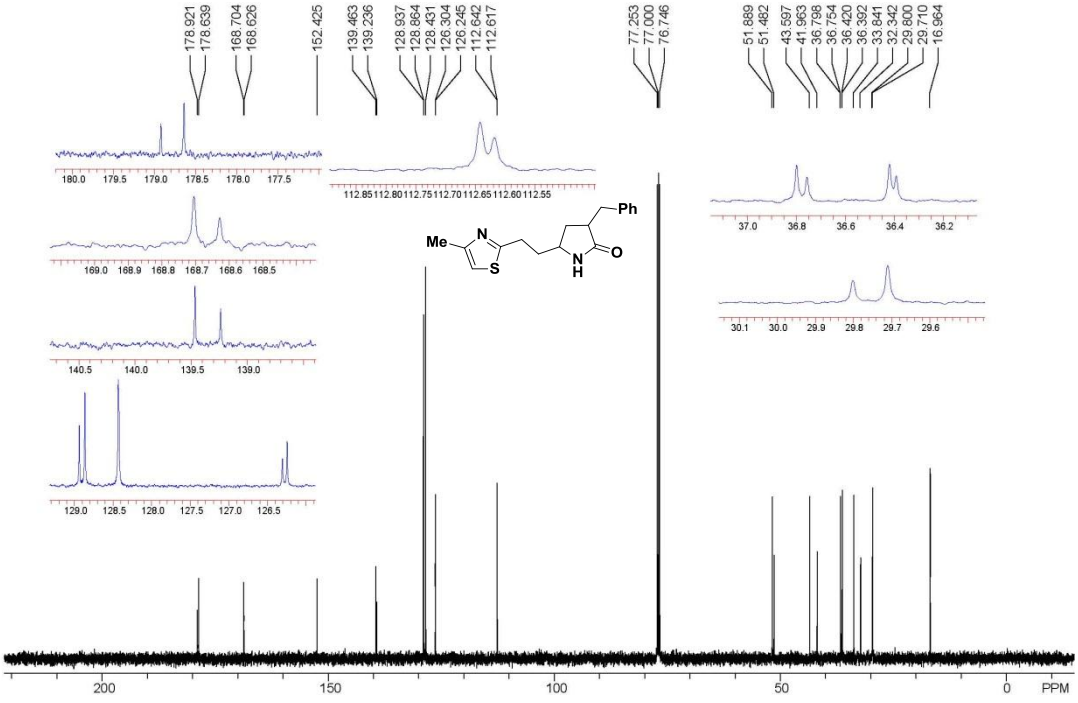
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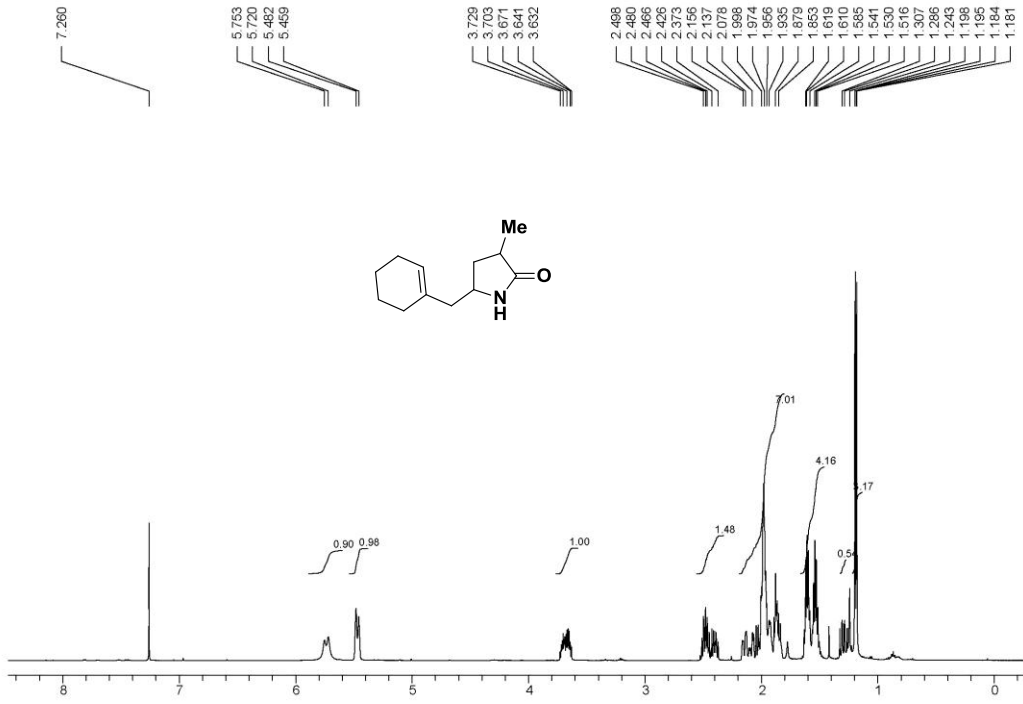
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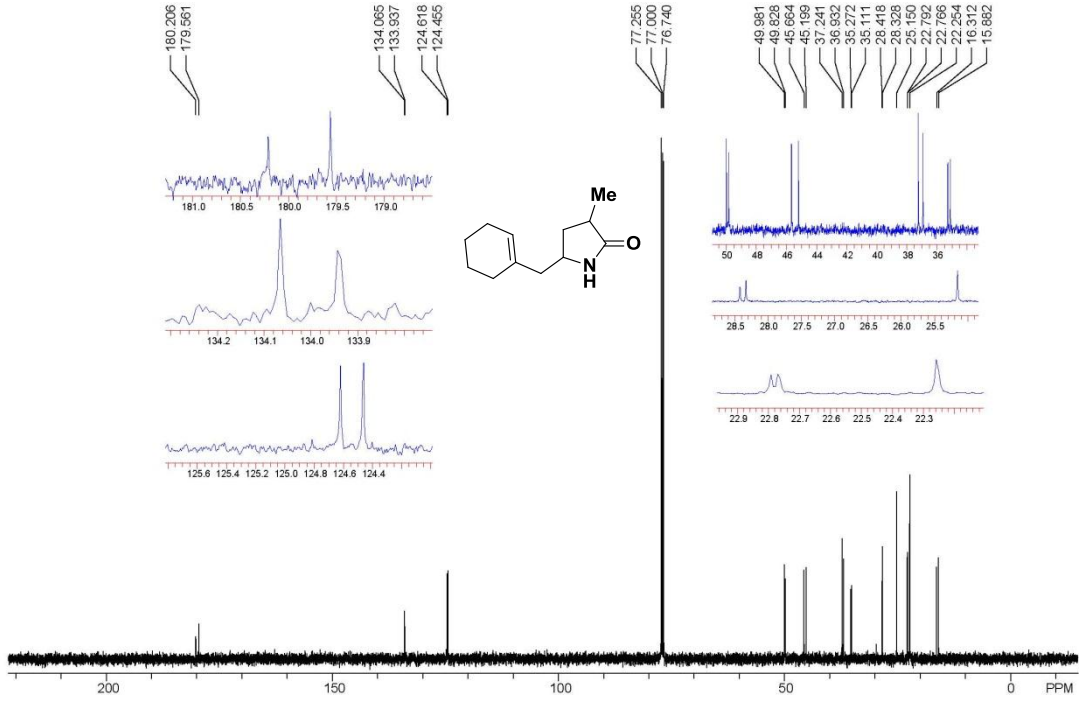
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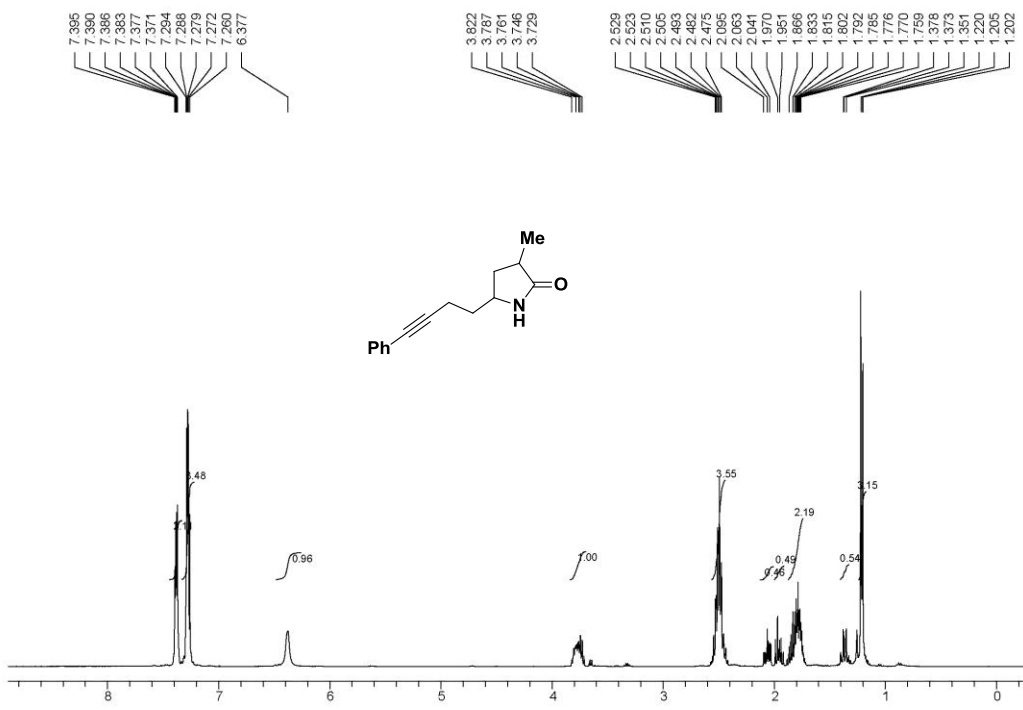
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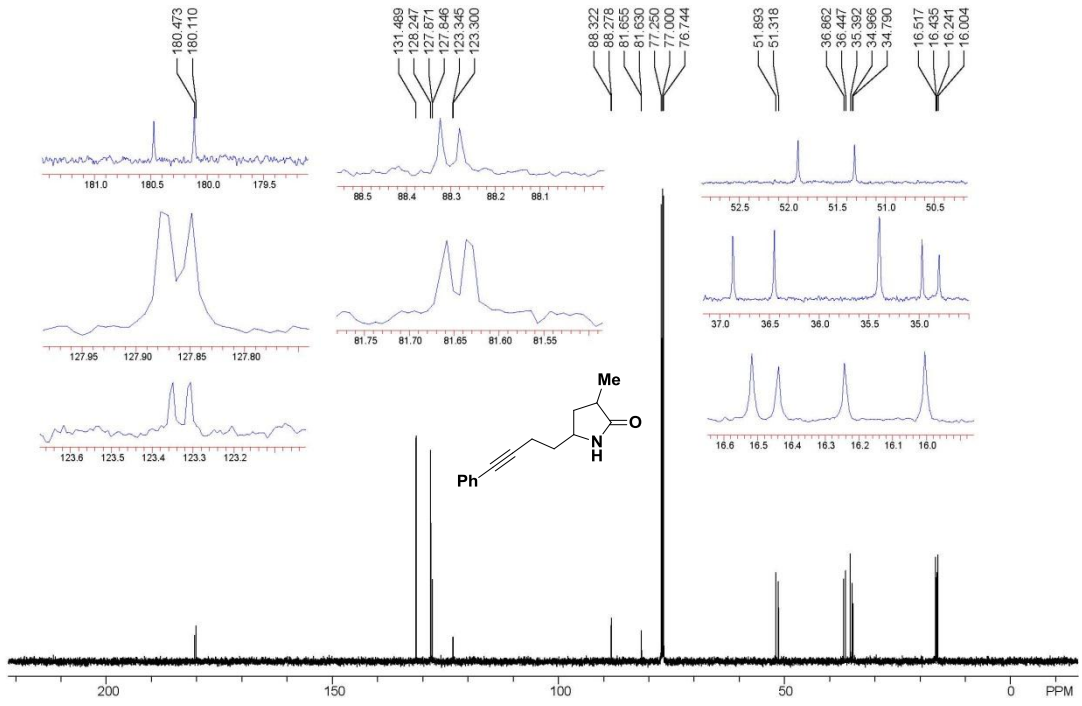
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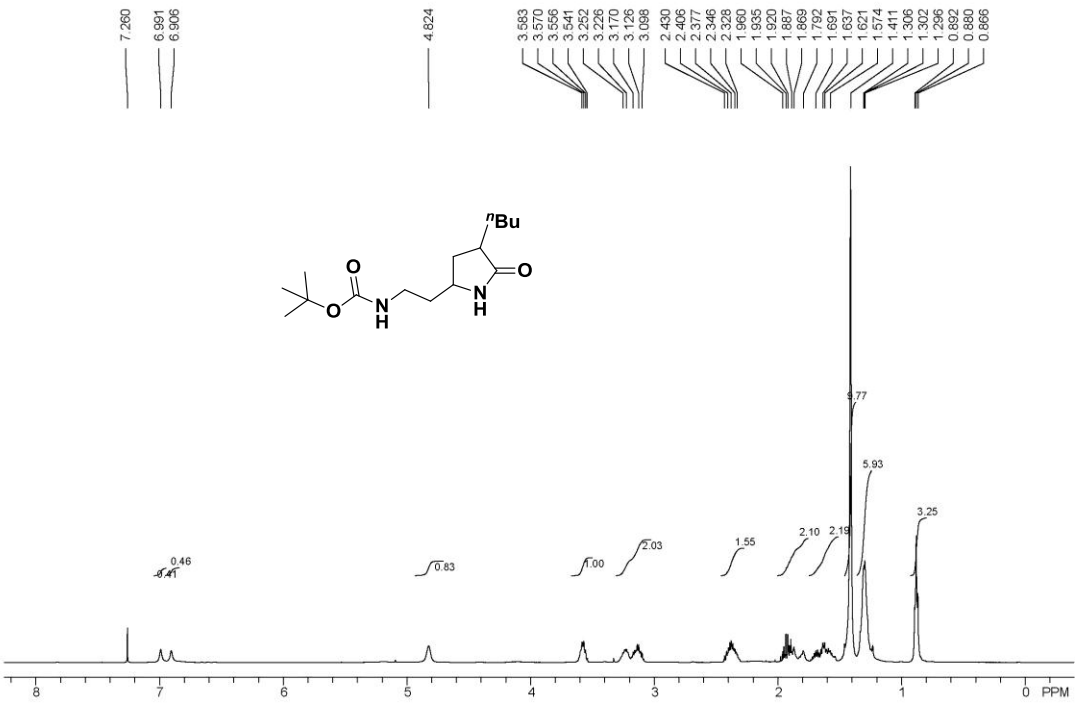
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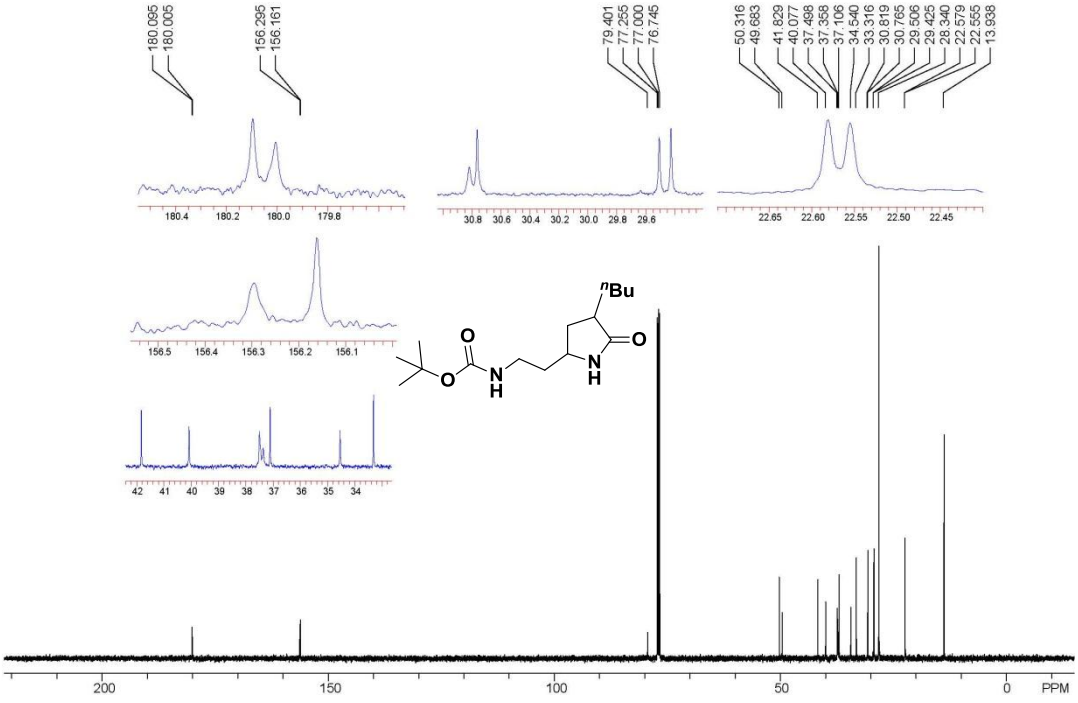
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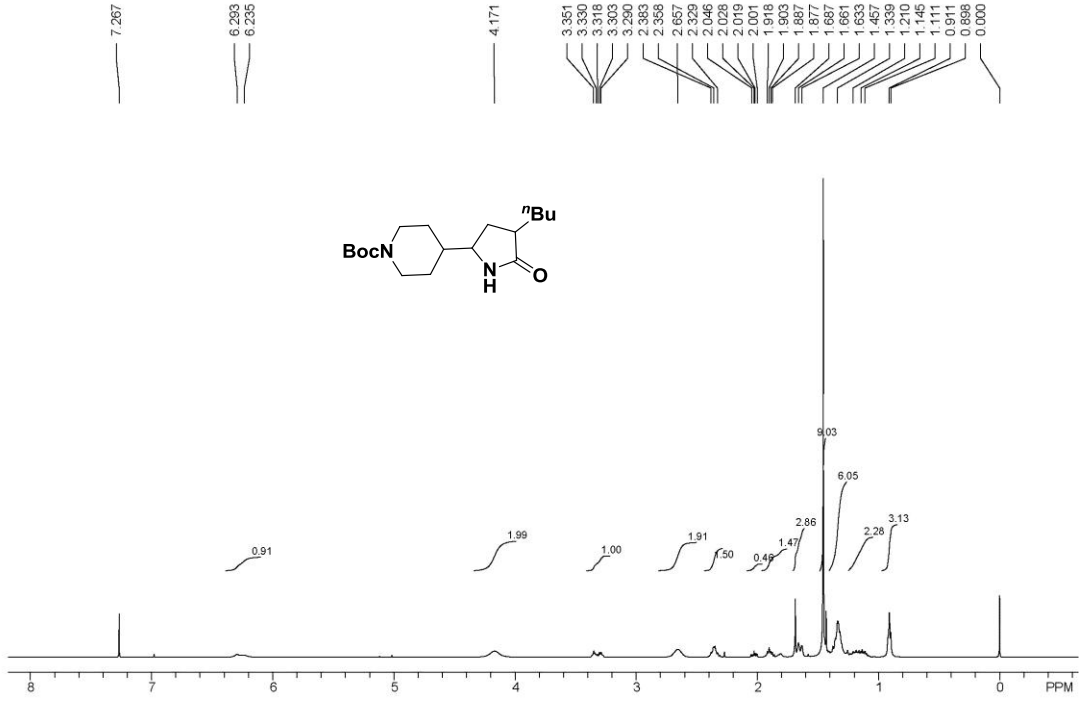
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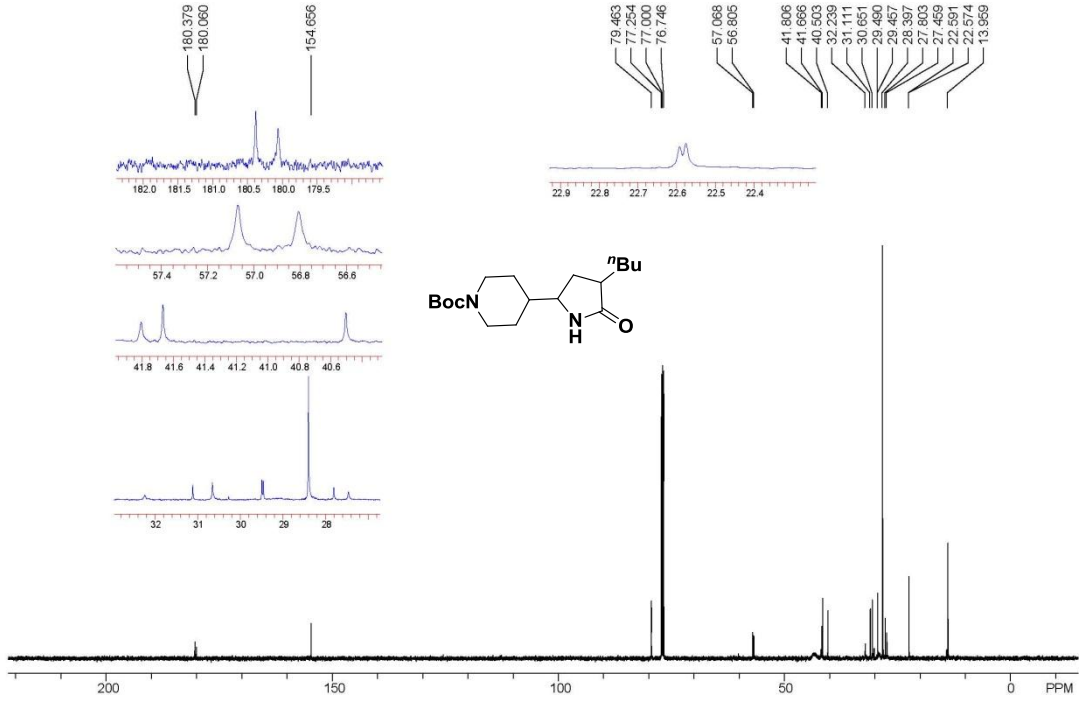
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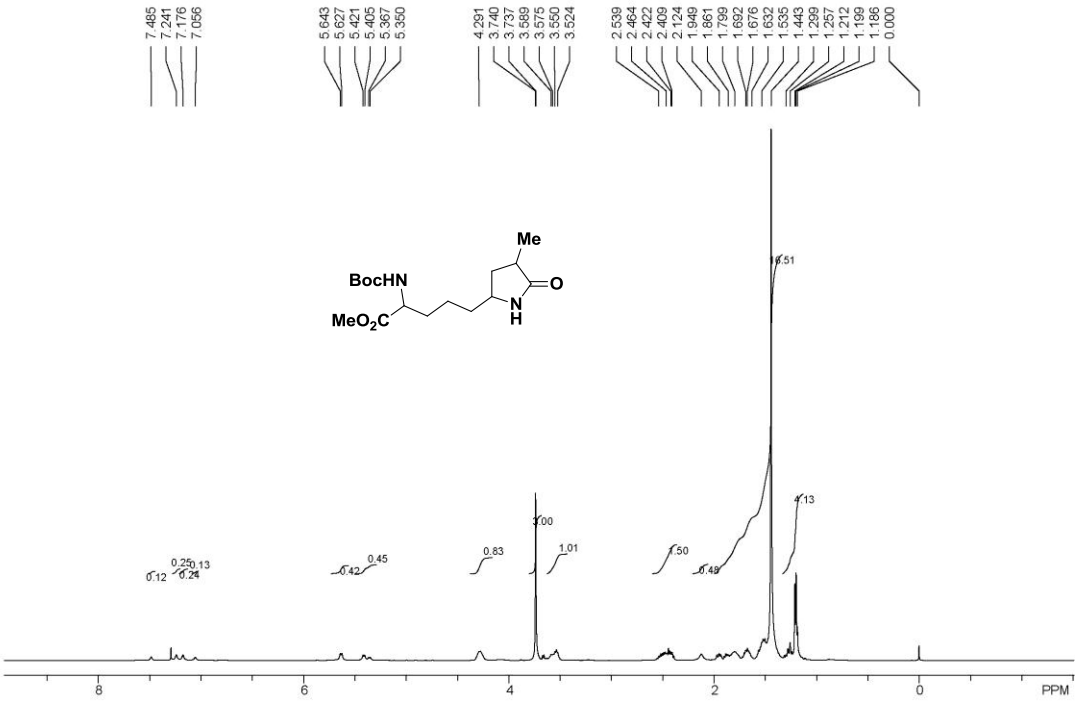
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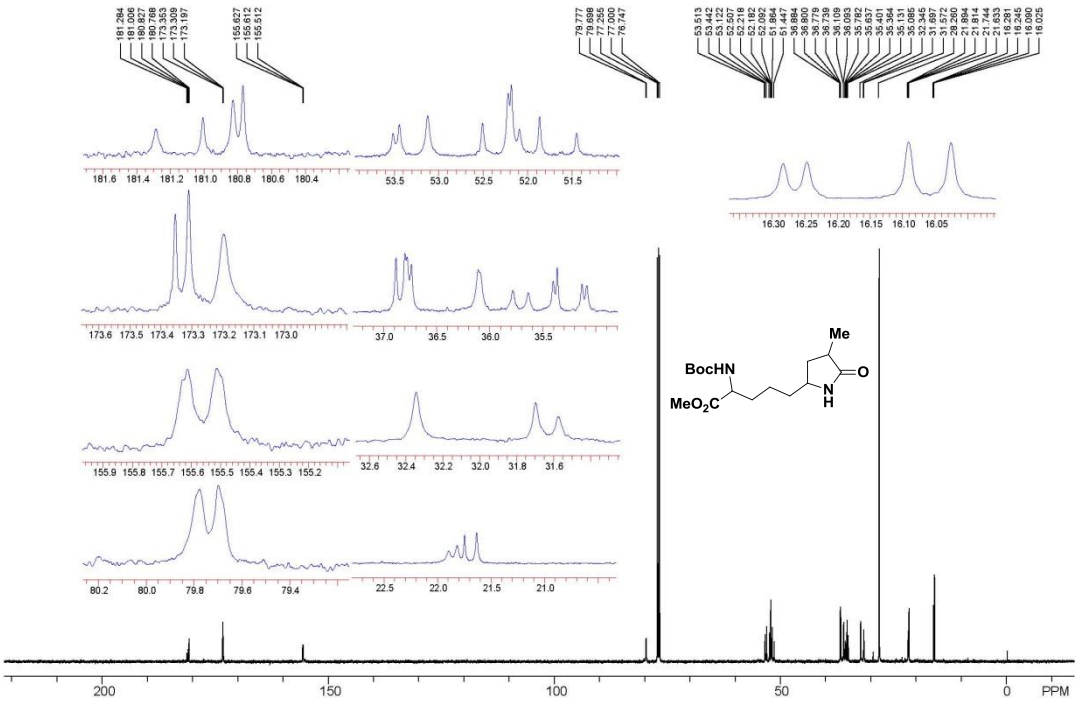
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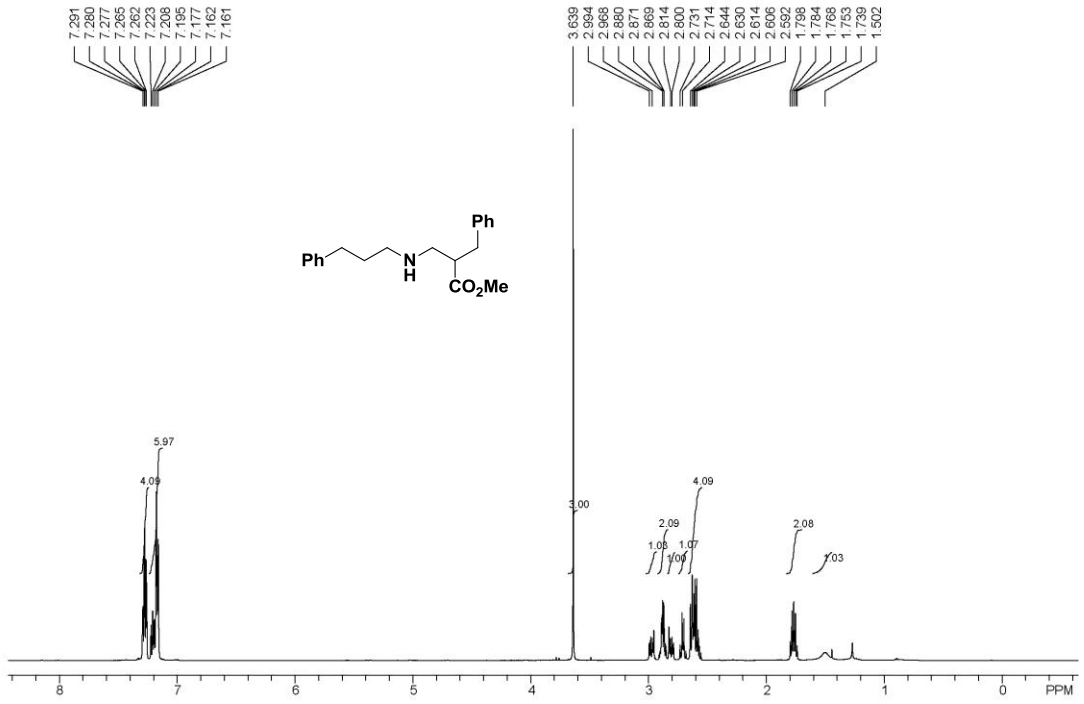
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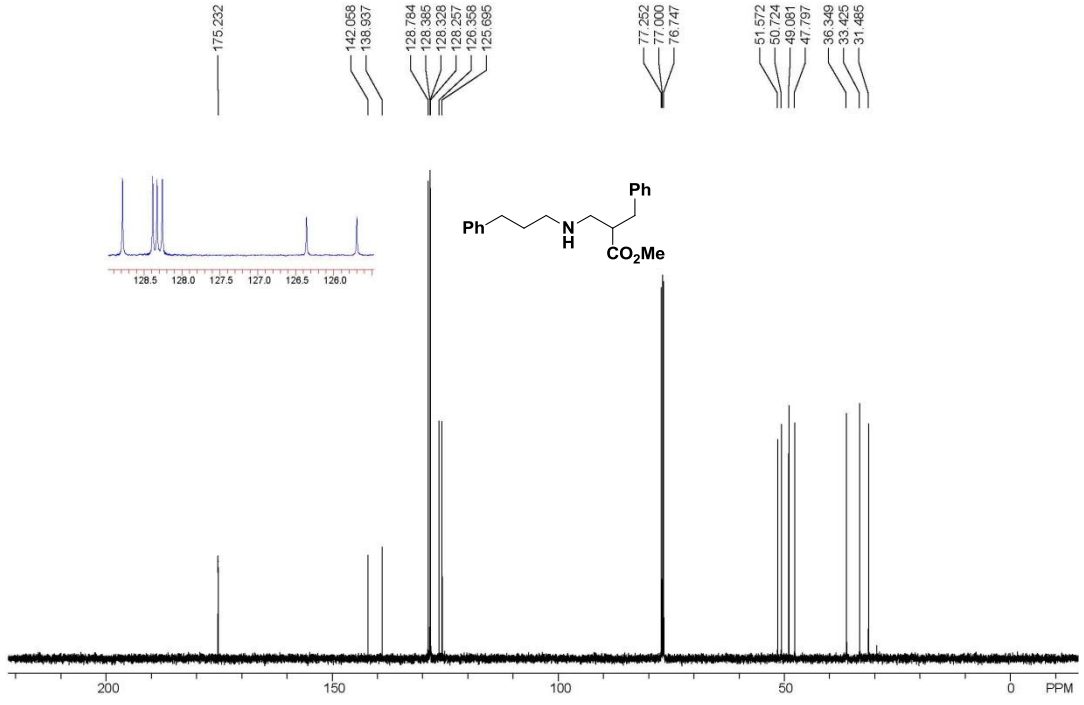
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H
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150
100
50
0
PPM

9. Computational details

General Information

Structure optimizations were performed using the M06L functional and 6-31+G(d,p) basis set on all atoms using Gaussian 09 program package.[8] Solvent effects of toluene were included in the optimization step using the CPCM solvation model. Frequency calculations were performed to confirm whether the structure is a minimum or a transition state. Intrinsic reaction coordinate (IRC) analysis was used to confirm that the obtained transition states connect the correct minima. All energies were corrected to 1M standard state with the addition of 1.89 kcal/mol to the energy of each species.[9] Free energies were computed after geometry optimization using Truhlar's quasiharmonic oscillator approximation, setting all frequencies below 100 to 100 cm^{-1}.[10] The quasiharmonic oscillator corrections were obtained using the GoodVibes.py program by Prof. Robert Paton.[11] Single point energies were calculated with the DLPNO-CCSD(T) method[12,13] and def2-TZVPD basis set on all atoms using ORCA 4.0 software.[14,15] CPCM solvation energies were calculated separately with CPCM (Toluene) at the M06-2X/def2-TZVPD level of theory ($E_{solv} = E_{CPCM}(M06\text{-}2X) - E_{GP}(M06\text{-}2X)$) with ORCA 4.0. Electronic energy of the hydrogen atom was calculated using the CCSD(T) approach with def2-TZVPD basis set using Gaussian 09.

Final free energy of a structure was obtained as follows:

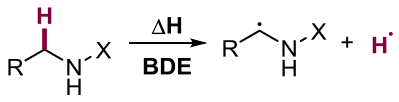
$$G = E(DLPNO) + G_{corr} + E_{solv}$$

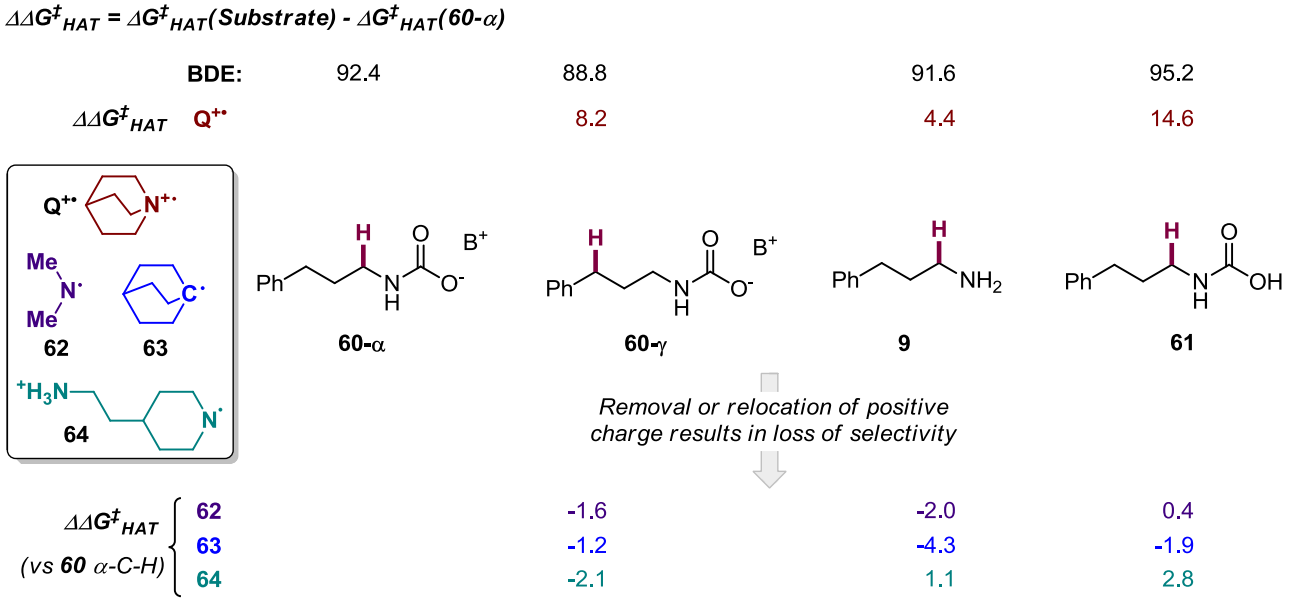
Additional density functional theory (DFT) methods were tested for both optimization as well as single point energy calculations. D3 corrections were applied using the D3BJ damping functions developed by Grimme and co-workers.[16]

DFT methods were tested for their ability to reproduce the zwitterionic nature of the ammonium carbamate structure in the starting material, and in its associated transition states. M06L, along with the inclusion of CPCM solvation model for toluene, was found to perform best in the geometry optimization.

Full data from the computational study shown in Fig. 4C

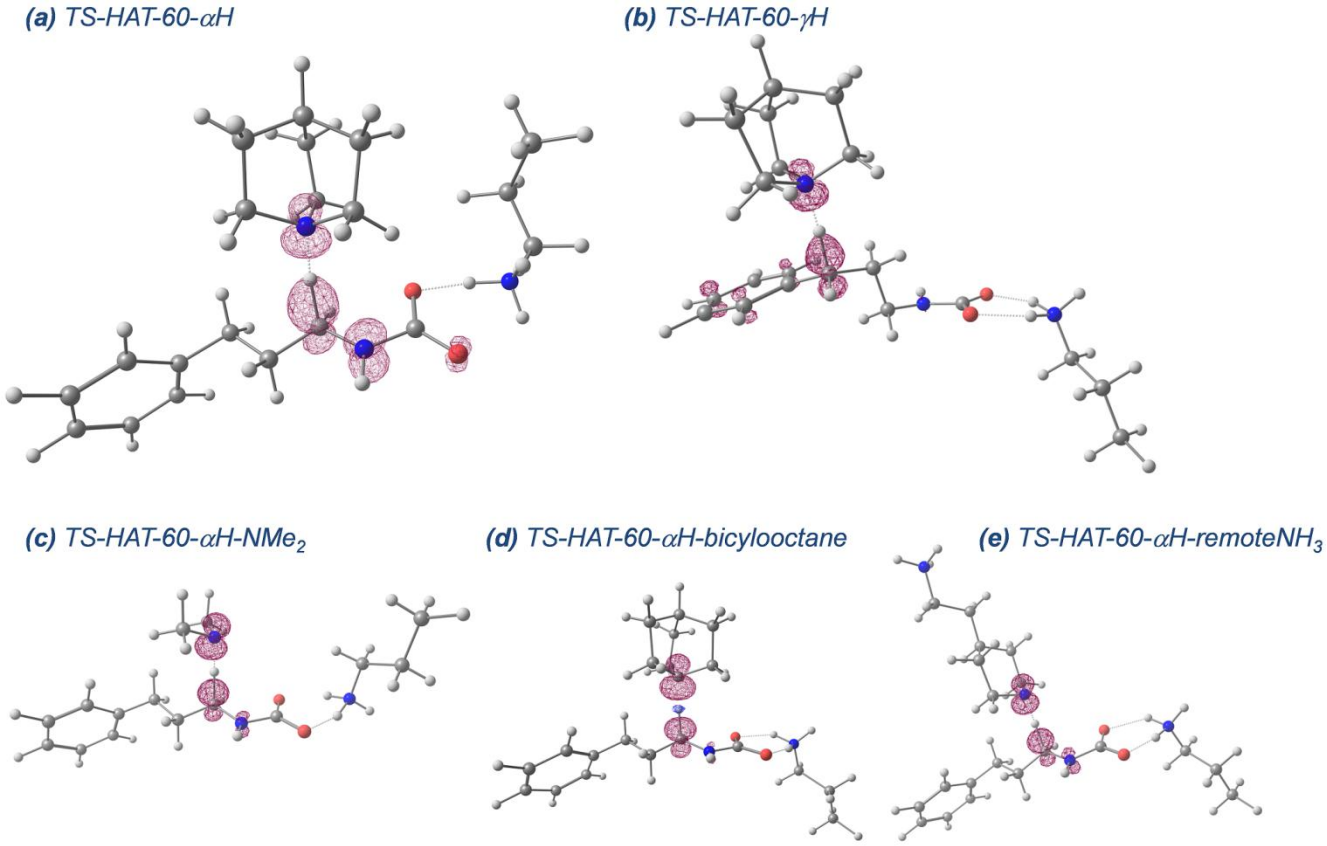
Bond dissociation energy was calculated as follows:





Supplementary Fig. 6. Comparison of bond dissociation energies and relative barriers for amine **9** and its derivatives (ammonium carbamate **60** and carbamic acid **61**). Calculated at the CPCM (Toluene) DLPNO-CCSD(T)/def2-TZVPD // CPCM (Toluene) M06L/6-31+G(d,p) level of theory. Free energies are shown in kcal/mol. B^+ = *n*-$C_3H_7NH_3^+$.

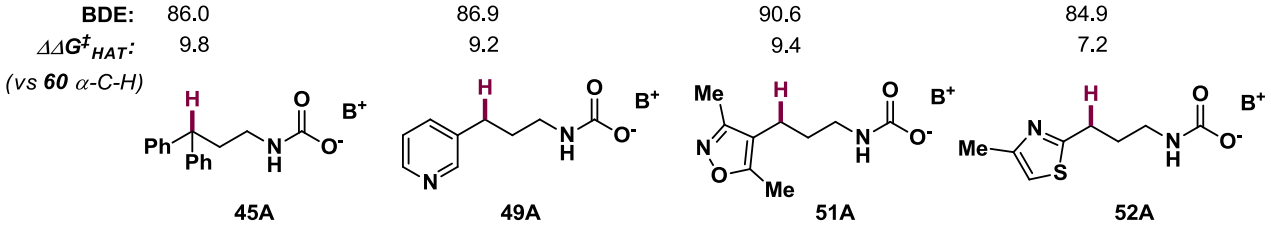
Spin density analysis of the HAT transition states



Supplementary Fig. 7. Spin density analyses of located HAT transition states of ammonium carbamate **60** with quinuclidinium radical cation (a and b); (c) HAT with hypothetical NMe_2 radical **62**; (d) HAT with hypothetical bicylo[2.2.2]octyl radical **63**; (e) HAT with hypothetical piperidine N-radical **64**. Calculated at the CPCM (Toluene) M06/def2-QZVP // CPCM (Toluene) M06L/6-31+G(d,p) level of theory.

Thermodynamic and kinetic descriptors of other amine substrates

Other amine substrates that contain benzylic hydrogens were also compared for their α-C–H *vs* benzylic C–H atom abstraction thermodynamic trends, as well as HAT reaction activation barriers (with quinuclidinium radical cation). The obtained data support the observation that bond dissociation energy (BDE) would suggest the benzylic site to be more reactive, in contrast to experimental observations shown in Fig. 3, which show high α-C–H selectivity. The activation barriers on the other hand are all in clear agreement with experimental results, clearly favoring the α-C–H site.

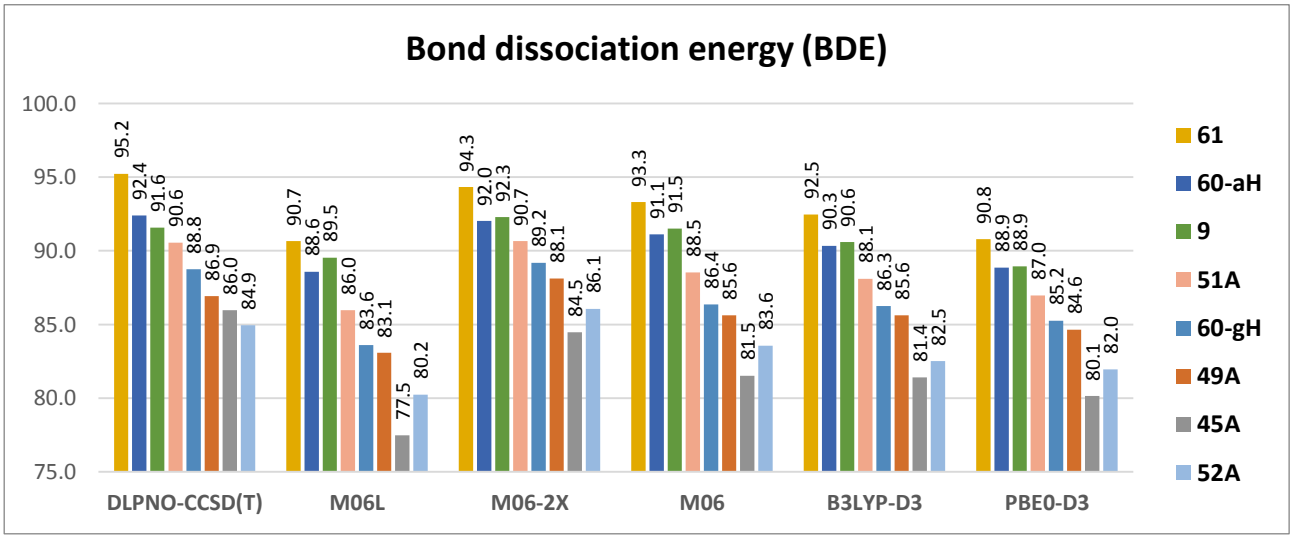


Supplementary Fig. 8. Comparison of BDE's and relative barriers (compared with that of **60** α-C–H) for ammonium carbamate structures based on other amines containing benzylic hydrogens. Calculated at the CPCM (Toluene) DLPNO-CCSD(T)/def2-TZVPD // CPCM (Toluene) M06L/6-31+G(d,p) level of theory. Free energies are shown in kcal/mol. B^+ = *n*-C_3H_7-NH_3^+.

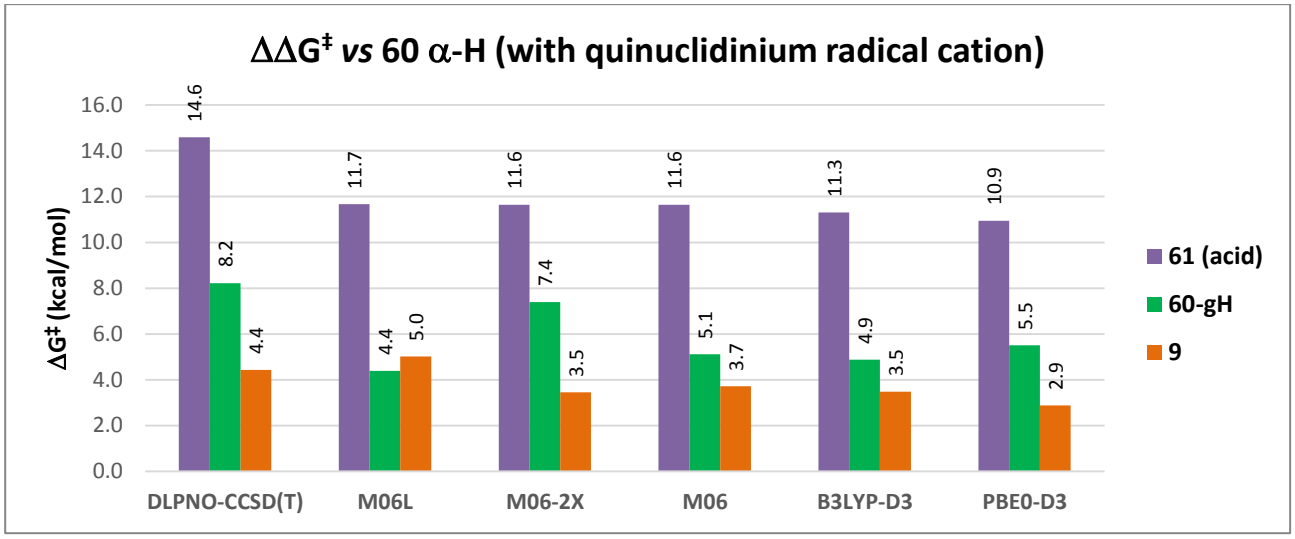
Comparison between DLPNO-CCSD(T) and various DFT methods

Various DFT methods were compared for their ability to reproduce the thermodynamic parameters and absolute barriers obtained at the CPCM (Toluene) DLPNO-CCSD(T) level of theory. DFT calculations were performed with Gaussian09 software using M06L, M06-2X, M06, B3LYP-D3 and PBE0-D3 methods along with def2-QZVP basis set and CPCM solvation model (toluene) for energies.

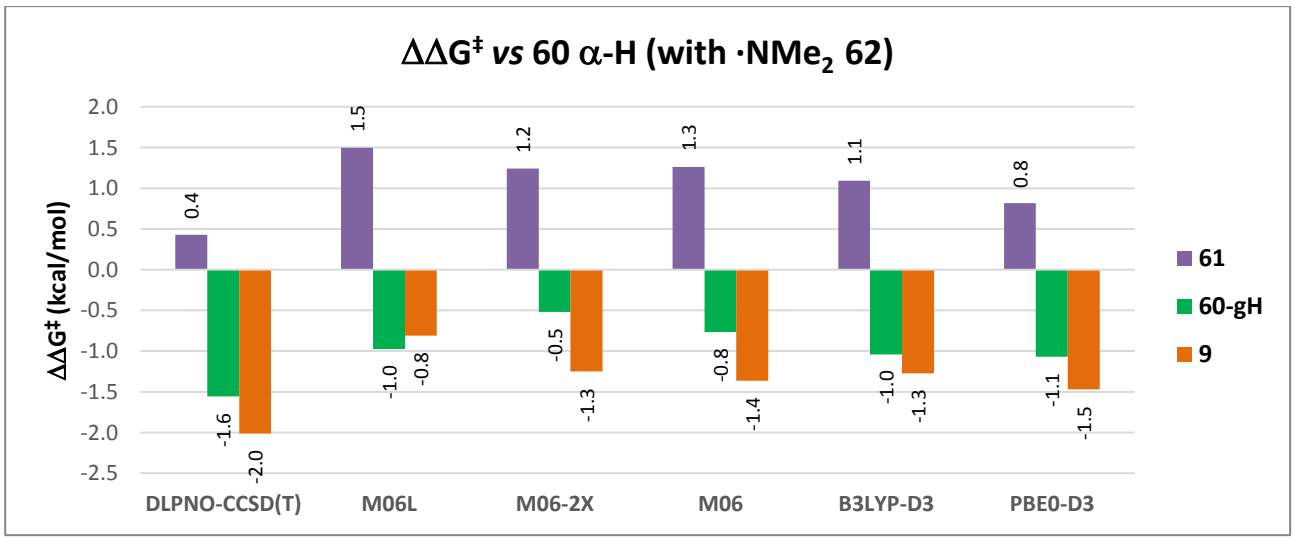
The obtained data suggest that, in relative terms, various DFT methods agree with each other quite well, and also with DLPNO-CCSD(T). Only M06L as a single point energy method shows in some cases different reactivity orders. However, all methods still suggest identical conclusions: (1) bond dissociation energy does not explain selectivity and the role of CO_2; (2) activation barriers suggest that α-C–H of the ammonium carbamate is the most reactive site; (3) removal of electrostatic interactions results in loss of selectivity.



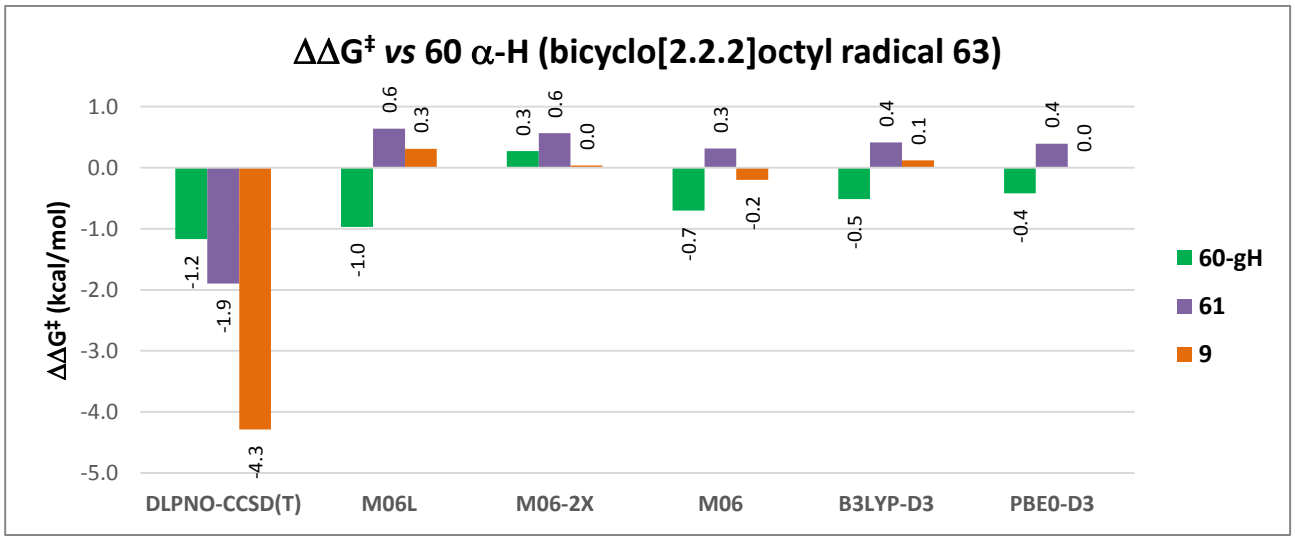
Supplementary Fig. 9. Comparison between DLPNO-CCSD(T) and various DFT methods for the calculation of BDEs of α-C–H bond of **9**, **60** and **61**, and of γ-C−H bond of **45A**, **49A**, **51A**, **52A**, and **60**.



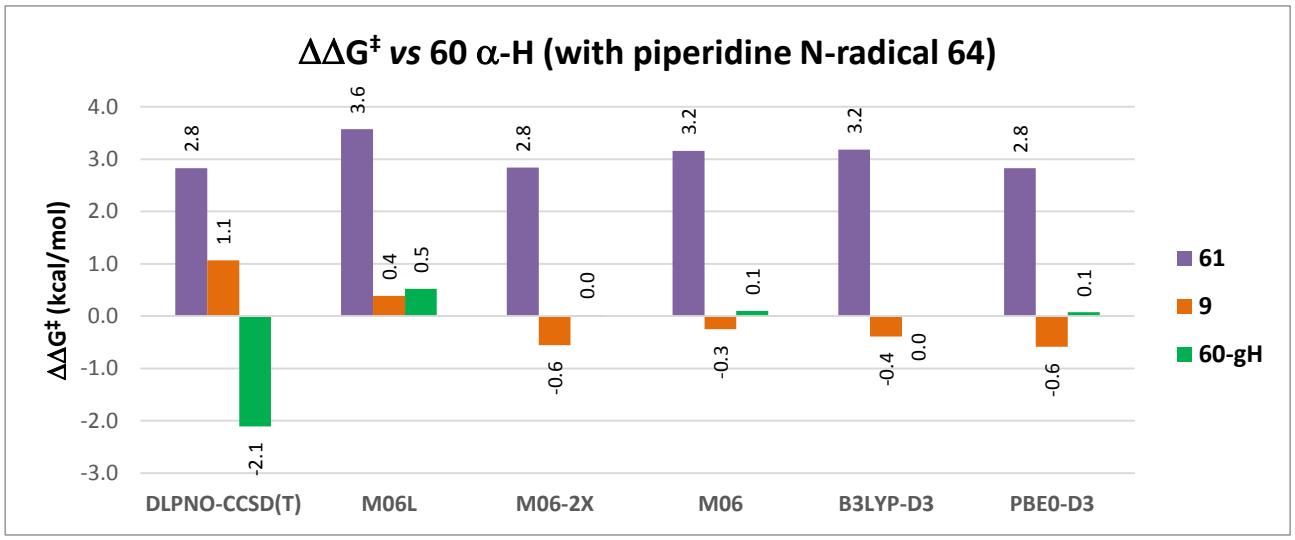
Supplementary Fig. 10. Comparison between DLPNO-CCSD(T) and various DFT methods for the calculation of activation barriers with quinuclidinium radical cation.



Supplementary Fig. 11. Comparison between DLPNO-CCSD(T) and various DFT methods for the calculation of activation barriers with hypothetical NMe_2 radical **62**.



Supplementary Fig. 12. Comparison between DLPNO-CCSD(T) and various DFT methods for the calculation of activation barriers with bicylo[2.2.2]octyl radical **63**.



Supplementary Fig. 13. Comparison between DLPNO-CCSD(T) and various DFT methods for the calculation of activation barriers with hypothetical piperidine N-radical **64**.

Energies and thermal data of computed structures

All values are reported in hartrees. G_corr = free energy correction, including the quasiharmonic correction. H_corr = enthalpy correction, without the quasiharmonic correction.

Structure	G_corr	H_corr	E(M06L)	E(M06-2X)	E(M06)	E(B3LYP_D3)	E(PBE0_D3)	E(DLPNO)	E_solv
9	0.168286	0.21428	-405.657299	-405.540534	-405.408635	-405.766600	-405.242384	-404.771156	-0.006402
60	0.296301	0.362136	-768.868789	-768.656743	-768.452163	-769.063121	-768.108356	-767.277121	-0.019287
61	0.180637	0.232393	-594.319414	-594.167538	-594.009812	-594.459929	-593.736991	-593.112892	-0.010983
9-aR	0.153476	0.200138	-405.002163	-404.885851	-404.753983	-405.111027	-404.590565	-404.116760	-0.006200
60-aR	0.282395	0.348807	-768.216005	-768.003295	-767.798948	-768.408760	-767.457474	-766.621656	-0.019627
61-aR	0.165733	0.218194	-593.662437	-593.509568	-593.352255	-593.801323	-593.082180	-592.452436	-0.010950
H atom	-0.01065	0.00236	-0.503672056	-0.498833212	-0.500046416	-0.502420487	-0.501303651	*-0.4998098*	-0.000101
Quinuclidine_rad_cat	0.163954		-329.178884	-329.070972	-328.973516	-329.262143	-328.845359	-328.414013	-0.049478
Quinuclidine_H+	0.181336		-329.839039	-329.738923	-329.637737	-329.927833	-329.508264	-329.080139	-0.052071
60-gR	0.284149	0.34941	-768.224507	-768.008420	-767.807136	-768.415876	-767.463835	-766.628551	-0.019139
TS_HAT_9_aH	0.352819		-734.848978	-734.625877	-734.395056	-735.046932	-734.107361	-733.202090	-0.046240
TS_HAT_60_aH	0.484592		-1098.072258	-1097.750794	-1097.44844	-1098.352178	-1096.981002	-1095.72747	-0.050496
TS_HAT_61_aH	0.364865		-923.500212	-923.239543	-922.983293	-923.727485	-922.588820	-921.529683	-0.048474
TS_HAT_60_gH	0.481188		-1098.061851	-1097.736186	-1097.436719	-1098.341605	-1096.969515	-1095.710196	-0.051300
TS_HAT_9_aH_NMe2	0.237694		-540.192446	-540.022082	-539.860163	-540.338452	-539.637555	-539.009314	-0.008216
TS_HAT_60_aH_NMe2	0.367712		-903.404641	-903.138296	-902.903514	-903.634942	-902.503181	-901.513902	-0.021267
TS_HAT_61_aH_NMe2	0.249642		-728.850480	-728.644714	-728.456752	-729.027610	-728.128112	-727.346564	-0.012992
TS_HAT_60_gH_NMe2	0.367741		-903.406225	-903.139157	-902.904772	-903.636633	-902.504917	-901.516575	-0.021109
TS_HAT_9_aH_remoteNH3	0.388286		-791.402371	-791.158863	-790.920637	-791.615578	-790.602706	-789.622683	-0.068650
TS_HAT_60_aH_remoteNH3	0.518562		-1154.616729	-1154.276440	-1153.966019	-1154.913734	-1153.469999	-1152.135286	-0.078849
TS_HAT_61_aH_remoteNH3	0.401746		-980.060507	-979.781555	-979.517485	-980.304320	-979.092974	-977.962418	-0.073522
TS_HAT_60_gH_remoteNH3	0.519566		-1154.616901	-1154.277411	-1153.966865	-1154.914771	-1153.470885	-1152.138579	-0.079920
TS_HAT_9_aH_BiCyOct	0.349123		-718.3532751	-718.1348541	-717.9037875	-718.550476	-717.6240453	-716.7634869	-0.006292
TS_HAT_60_aH_ BiCyOct	0.478531		-1081.566648	-1081.252513	-1080.948388	-1081.848586	-1080.491427	-1079.264144	-0.019047
TS_HAT_61_aH_ BiCyOct	0.361514		-907.0149038	-906.761054	-906.5041855	-907.2433816	-906.1180779	-905.101553	-0.010771
TS_HAT_60_gH_ BiCyOct	0.479589		-1081.569247	-1081.253137	-1080.950568	-1081.850465	-1080.493149	-1079.266683	-0.019426
45A	0.374775	0.448757	-999.981971	-999.712434	-999.420493	-1000.235791	-998.988834	-997.877503	-0.021607
49A	0.285919	0.351182	-784.912342	-784.699100	-784.496073	-785.105269	-784.140207	-783.306870	-0.020890
51A	0.307857	0.378552	-861.341846	-861.102544	-860.899129	-861.542840	-860.498949	-859.607574	-0.022185
52A	0.278358	0.34665	-1145.020774	-1144.801959	-1144.615182	-1145.224688	-1144.155804	-1143.016178	-0.020421
45A-gR	0.361633	0.436012	-999.347455	-999.071605	-998.783155	-999.596257	-998.352429	-997.233851	-0.020971
49A-gR	0.272745	0.337693	-784.268175	-784.051708	-783.851465	-784.458281	-783.495908	-782.660568	-0.020645
51A-gR	0.293527	0.364636	-860.692617	-860.450682	-860.249440	-860.891472	-859.850509	-858.955428	-0.021566
52A-gR	0.265244	0.333417	-1144.381383	-1144.158115	-1143.974133	-1144.582912	-1143.516047	-1142.373544	-0.019927
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TS_HAT_51A_gH	0.493372							-1188.03829	-0.055199
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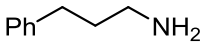
XYZ coordinates of computed structures



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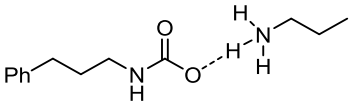

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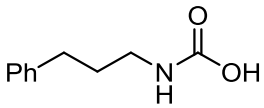

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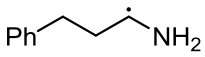
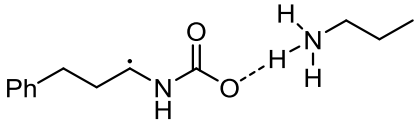
O	3.450243000000	1.307113000000	0.601011000000
H	5.017074000000	1.323351000000	-1.087040000000
C	-1.924312000000	-0.299707000000	0.450708000000
C	-2.312406000000	1.031411000000	0.642091000000
C	-2.752202000000	-1.129824000000	-0.313116000000
C	-3.494079000000	1.519810000000	0.088951000000
C	-3.935470000000	-0.646429000000	-0.868756000000
C	-4.310448000000	0.681325000000	-0.669572000000
H	-1.678800000000	1.689210000000	1.234722000000
H	-2.464702000000	-2.168517000000	-0.469276000000
H	-3.779770000000	2.555621000000	0.252709000000
H	-4.567001000000	-1.308496000000	-1.455330000000
H	-5.234322000000	1.059005000000	-1.098721000000



9-aR

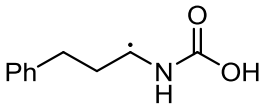
N	-4.219944000000	0.025238000000	-0.726531000000
H	-5.148707000000	0.157942000000	-0.350187000000
H	-4.039336000000	0.712162000000	-1.448426000000
C	-3.213454000000	-0.055312000000	0.244065000000
H	-3.475144000000	-0.657700000000	1.113585000000
C	-1.802368000000	-0.058642000000	-0.219572000000
H	-1.633594000000	0.774735000000	-0.920557000000
H	-1.565880000000	-0.969474000000	-0.803923000000
C	-0.803940000000	0.048601000000	0.936106000000
H	-0.983572000000	-0.781377000000	1.632039000000
H	-1.002355000000	0.971484000000	1.494407000000
C	0.623781000000	0.024644000000	0.470182000000
C	1.328420000000	1.213207000000	0.249958000000
C	1.267592000000	-1.188408000000	0.197150000000
C	2.638520000000	1.193720000000	-0.226243000000
C	2.576579000000	-1.214331000000	-0.279560000000
C	3.267341000000	-0.021546000000	-0.493125000000
H	0.841242000000	2.164290000000	0.458676000000
H	0.733502000000	-2.122278000000	0.365531000000
H	3.169638000000	2.128382000000	-0.386171000000
H	3.059808000000	-2.166721000000	-0.481325000000
H	4.289179000000	-0.039712000000	-0.861697000000



60-aR

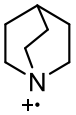
N	0.661203000000	-0.542405000000	-0.506036000000
H	0.487211000000	-0.431663000000	-1.494599000000
C	-0.411421000000	-0.609020000000	0.363267000000

H	-0.139576000000	-0.650292000000	1.412861000000
C	-1.740039000000	-0.131150000000	-0.088154000000
H	-1.942005000000	-0.478749000000	-1.114043000000
H	-1.783363000000	0.974198000000	-0.152666000000
C	-2.873109000000	-0.601555000000	0.829131000000
H	-2.664947000000	-0.256110000000	1.849869000000
H	-2.868157000000	-1.697617000000	0.863701000000
C	1.995839000000	-0.745524000000	-0.157800000000
O	2.820021000000	-0.707733000000	-1.141538000000
O	2.276039000000	-0.937197000000	1.055944000000
N	4.879957000000	-1.029902000000	0.376846000000
H	4.182004000000	-1.232260000000	1.112179000000
H	5.536398000000	-1.798860000000	0.272844000000
H	4.186051000000	-0.956181000000	-0.458012000000
C	5.552461000000	0.268982000000	0.609769000000
H	4.753384000000	0.996296000000	0.783560000000
H	6.143877000000	0.200823000000	1.527883000000
C	6.407647000000	0.671772000000	-0.574482000000
H	5.779694000000	0.704168000000	-1.473037000000
H	7.168142000000	-0.098957000000	-0.755250000000
C	7.074647000000	2.017252000000	-0.350430000000
H	7.723845000000	1.999865000000	0.530838000000
H	6.332413000000	2.806907000000	-0.198034000000
H	7.688742000000	2.302335000000	-1.207301000000
C	-4.218301000000	-0.104134000000	0.384538000000
C	-5.012868000000	-0.863330000000	-0.482022000000
C	-4.688296000000	1.151586000000	0.786790000000
C	-6.242316000000	-0.385950000000	-0.932612000000
C	-5.916623000000	1.634378000000	0.339468000000
C	-6.698800000000	0.865805000000	-0.522056000000
H	-4.660138000000	-1.842272000000	-0.803060000000
H	-4.082088000000	1.753745000000	1.461800000000
H	-6.846584000000	-0.993751000000	-1.601016000000
H	-6.266093000000	2.610120000000	0.667197000000
H	-7.658339000000	1.239159000000	-0.869068000000



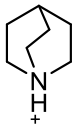
61-aR

N	-2.837099000000	0.347294000000	-0.327923000000
H	-2.653531000000	1.097566000000	-0.979615000000
C	-1.778842000000	-0.236253000000	0.348728000000
H	-2.049641000000	-1.072498000000	0.983675000000
C	-0.395297000000	0.004148000000	-0.118424000000
H	-0.266839000000	1.059222000000	-0.406129000000
H	-0.174080000000	-0.570084000000	-1.037843000000
C	0.648150000000	-0.360291000000	0.942395000000
H	0.495072000000	-1.405453000000	1.239763000000
H	0.473754000000	0.248363000000	1.837325000000
C	-4.143298000000	0.020744000000	-0.109958000000
O	-4.954910000000	0.799380000000	-0.874769000000
O	-4.539857000000	-0.842553000000	0.656647000000
H	-5.859970000000	0.522344000000	-0.678993000000
C	2.053550000000	-0.168168000000	0.448497000000
C	2.694013000000	-1.170676000000	-0.289119000000
C	2.735387000000	1.033151000000	0.670229000000
C	3.979361000000	-0.980243000000	-0.791295000000
C	4.021647000000	1.228890000000	0.170587000000
C	4.647911000000	0.221954000000	-0.562470000000
H	2.176838000000	-2.112449000000	-0.466805000000
H	2.250032000000	1.820877000000	1.244140000000
H	4.461942000000	-1.772333000000	-1.357607000000
H	4.536981000000	2.167450000000	0.357580000000
H	5.651775000000	0.371788000000	-0.950088000000



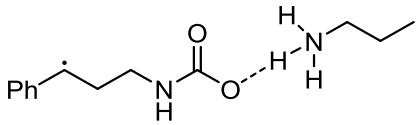
Quinuclidinium_rad_cat

N	0.006767000000	0.068150000000	1.159766000000
C	0.254224000000	-1.326689000000	0.891861000000
C	0.969706000000	1.010163000000	-0.821906000000
C	-0.007522000000	-0.074255000000	-1.267861000000
C	0.423689000000	-1.413910000000	-0.676772000000
C	1.072347000000	0.950178000000	0.753702000000
H	-0.597434000000	-1.911625000000	1.241024000000
H	1.161314000000	-1.645205000000	1.408211000000
H	0.625080000000	2.001964000000	-1.124742000000
H	1.969304000000	0.855679000000	-1.234450000000
H	-0.014149000000	-0.138301000000	-2.361710000000
H	-0.191917000000	-2.239669000000	-1.040642000000
H	1.466817000000	-1.634642000000	-0.916399000000
H	0.924963000000	1.934830000000	1.200269000000
H	2.024075000000	0.531368000000	1.082278000000
C	-1.312226000000	0.519965000000	0.792840000000
H	-1.407023000000	1.577788000000	1.040831000000
H	-2.063001000000	-0.057931000000	1.334255000000
C	-1.406606000000	0.270546000000	-0.764662000000
H	-1.798391000000	1.176883000000	-1.231940000000
H	-2.108675000000	-0.544173000000	-0.958558000000



Quinuclidine_H

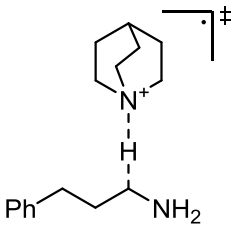
N	1.225074000000	-0.000188000000	0.001366000000
C	0.735184000000	0.286563000000	-1.400326000000
C	-0.775647000000	0.882615000000	1.134080000000
C	-1.304001000000	0.000102000000	-0.001210000000
C	-0.773324000000	0.541324000000	-1.332420000000
C	0.732667000000	1.070151000000	0.949075000000
H	0.995449000000	-0.589801000000	-1.998120000000
H	1.304969000000	1.139210000000	-1.772663000000
H	-0.989258000000	0.420078000000	2.102442000000
H	-1.264322000000	1.859605000000	1.130571000000
H	-2.395638000000	0.000154000000	-0.002381000000
H	-1.261030000000	0.050164000000	-2.177521000000
H	-0.986034000000	1.611331000000	-1.416423000000
H	1.301283000000	0.967777000000	1.874534000000
H	0.992500000000	2.026091000000	0.488838000000
C	0.733080000000	-1.356648000000	0.453050000000
H	0.991745000000	-1.436501000000	1.511277000000
H	1.303153000000	-2.106020000000	-0.098202000000
C	-0.774881000000	-1.423953000000	0.196224000000
H	-1.264138000000	-1.910032000000	1.043398000000
H	-0.986772000000	-2.031435000000	-0.688832000000
H	2.244101000000	-0.000231000000	0.002687000000



60-gR

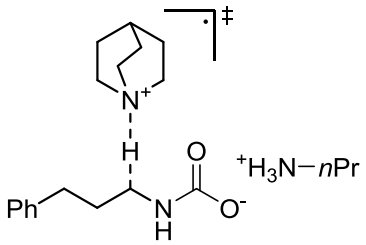
N	-0.469721000000	-1.378195000000	-0.622620000000
H	-0.238987000000	-2.354689000000	-0.725432000000
C	0.612428000000	-0.427374000000	-0.565506000000
H	1.337245000000	-0.672684000000	-1.350714000000
H	0.207376000000	0.562134000000	-0.794676000000
C	1.332965000000	-0.372224000000	0.799821000000
H	1.744618000000	-1.367522000000	1.015226000000
H	0.573214000000	-0.169015000000	1.562181000000
C	2.390142000000	0.668846000000	0.835549000000
H	2.106164000000	1.669438000000	1.163486000000
C	3.713544000000	0.503695000000	0.364059000000
C	4.620150000000	1.600799000000	0.380848000000
C	4.202670000000	-0.732147000000	-0.144973000000
C	5.918245000000	1.471764000000	-0.081264000000
C	5.504518000000	-0.851048000000	-0.605073000000
C	6.374576000000	0.244842000000	-0.579900000000
H	4.269176000000	2.556609000000	0.764934000000
H	3.542442000000	-1.595724000000	-0.175236000000
H	6.586063000000	2.329097000000	-0.058000000000
H	5.851572000000	-1.806457000000	-0.990331000000
H	7.393228000000	0.144755000000	-0.943759000000
C	-1.699282000000	-1.138094000000	-0.029236000000

O	-1.940657000000	0.056452000000	0.349977000000
O	-2.493738000000	-2.128431000000	0.055620000000
H	-3.967145000000	-1.478582000000	0.693861000000
N	-4.402951000000	-0.548484000000	0.926103000000
H	-4.817653000000	-0.543703000000	1.853868000000
H	-3.488073000000	-0.000043000000	0.889069000000
C	-5.336775000000	-0.089149000000	-0.125783000000
H	-4.813405000000	-0.226854000000	-1.077303000000
H	-6.208374000000	-0.750469000000	-0.131404000000
C	-5.738181000000	1.359128000000	0.068906000000
H	-4.833940000000	1.979761000000	0.089701000000
H	-6.216920000000	1.477275000000	1.049657000000
C	-6.675399000000	1.833763000000	-1.027399000000
H	-7.595317000000	1.240824000000	-1.050741000000
H	-6.205875000000	1.753284000000	-2.012713000000
H	-6.959152000000	2.878352000000	-0.881126000000



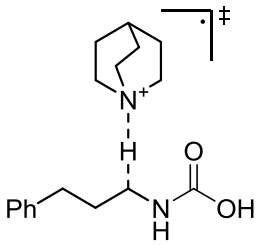
TS_HAT_9_aH

N	0.672916000000	3.182058000000	-0.816100000000
H	0.530335000000	3.059463000000	-1.808235000000
C	0.215056000000	2.220119000000	0.067429000000
H	1.101529000000	1.204455000000	0.098770000000
H	0.293746000000	2.559693000000	1.107577000000
C	-1.103301000000	1.578366000000	-0.288668000000
H	-1.065226000000	1.189122000000	-1.316442000000
H	-1.884022000000	2.352311000000	-0.292726000000
C	-1.507284000000	0.461631000000	0.673676000000
H	-1.496922000000	0.850126000000	1.700186000000
H	-0.758542000000	-0.341822000000	0.640468000000
H	1.442645000000	3.781187000000	-0.560342000000
C	3.325372000000	0.938867000000	-0.184415000000
N	2.038204000000	0.250220000000	0.089605000000
C	1.744151000000	-0.728914000000	-0.987295000000
C	2.088611000000	-0.432510000000	1.408648000000
C	4.421887000000	-0.115113000000	-0.425892000000
H	3.537192000000	1.572429000000	0.682385000000
H	3.172826000000	1.591514000000	-1.049337000000
C	3.890410000000	-1.473328000000	0.039481000000
C	2.747222000000	-1.895258000000	-0.887744000000
H	2.253921000000	-2.790047000000	-0.494847000000
H	3.124022000000	-2.146915000000	-1.882816000000
H	4.688674000000	-2.219324000000	0.017625000000
C	3.344657000000	-1.321955000000	1.462260000000
H	5.327090000000	0.159681000000	0.122257000000
H	4.688580000000	-0.156231000000	-1.486751000000
H	0.707413000000	-1.058406000000	-0.867840000000
H	1.818327000000	-0.189986000000	-1.937151000000
H	1.165790000000	-1.012515000000	1.502995000000
H	2.079733000000	0.337834000000	2.185009000000
H	3.090150000000	-2.295171000000	1.890528000000
H	4.105201000000	-0.874833000000	2.110533000000
C	-2.863092000000	-0.099940000000	0.347714000000
C	-3.004113000000	-1.124706000000	-0.594141000000
C	-4.014524000000	0.429776000000	0.938580000000
C	-4.264028000000	-1.609420000000	-0.938235000000
C	-5.276633000000	-0.051837000000	0.597436000000
C	-5.404638000000	-1.072661000000	-0.343022000000
H	-2.115915000000	-1.550179000000	-1.060381000000
H	-3.918758000000	1.224917000000	1.675954000000
H	-4.355860000000	-2.408832000000	-1.668157000000
H	-6.160662000000	0.368064000000	1.069202000000
H	-6.387630000000	-1.451192000000	-0.607877000000



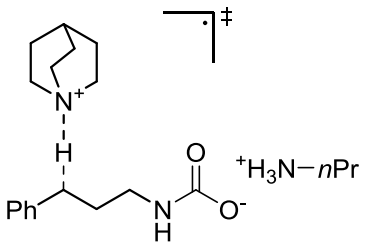
TS_HAT_60_aH

N	0.213370616924	1.983808246623	-0.639370473446
H	-0.073013230931	2.265122047255	-1.569017951766
C	-0.632028668293	1.221238430306	0.148753841403
H	-0.196502562935	-0.037406481377	0.071054745932
H	-0.404359152924	1.362292742736	1.213125613901
C	-2.089874946880	1.224256328157	-0.225926405511
H	-2.222029027159	0.835183518425	-1.245809717509
H	-2.456828147604	2.260729876088	-0.254444296637
C	-2.944068099621	0.415816369542	0.751219493503
H	-2.828565110659	0.837494435471	1.757318267342
H	-2.564573398096	-0.613468834639	0.802669809892
C	1.556763265034	2.298538002997	-0.288830763454
O	1.956814385974	1.808227235404	0.814191056957
O	2.188787699909	2.997786998876	-1.103933063634
C	1.568042148919	-1.181103511033	-0.824997385559
N	0.375420565885	-1.259076720318	0.055774223690
C	-0.559019141603	-2.301095516642	-0.438868918040
C	0.788146011116	-1.551564627740	1.451857579661
C	2.418886138851	-2.449645624804	-0.620403173310
H	2.107965400315	-0.266028515795	-0.564609370061
H	1.201777936974	-1.083287213264	-1.851427149304
C	1.560147882719	-3.493435577379	0.098236993682
C	0.223258822999	-3.614479581316	-0.638494155921
H	-0.361841348498	-4.455167072307	-0.255645528992
H	0.396105575371	-3.801050545641	-1.703590372073
H	2.071432061398	-4.459422715744	0.117091579063
C	1.293676974744	-3.003483062784	1.525330665621
H	3.307981706227	-2.222163967358	-0.021582494100
H	2.770431814793	-2.822989169986	-1.586630558145
H	-1.349416272736	-2.406241448486	0.310512742877
H	-1.016054185424	-1.934330173841	-1.362717142889
H	-0.075583974006	-1.373424515346	2.099527669079
H	1.555416508935	-0.814470991722	1.708237077497
H	0.552151479265	-3.646611753052	2.010841266388
H	2.203389816918	-3.049895082585	2.130523697262
H	4.214664479473	3.617459907582	0.060634716722
N	4.420486912117	2.762120556920	0.576932320659
H	4.997561581455	2.986142453512	1.385289198445
H	3.460007450560	2.389140027330	0.870557429989
C	5.063429331993	1.757525704823	-0.317214243559
H	4.399025070429	1.670382382990	-1.181528440363
H	6.017738586826	2.163696231470	-0.662409263335
C	5.238783326171	0.428971715952	0.389285538986
H	4.262930736354	0.095911788850	0.769384560930
H	5.884492813883	0.557477648277	1.266854567524
C	5.830183352818	-0.612736982503	-0.544720243158
H	6.810521248998	-0.302363942420	-0.918422570515
H	5.184812538546	-0.779070092118	-1.413932504579
H	5.960433453355	-1.571674950734	-0.038177492629
C	-4.395109158786	0.399519297805	0.361435998726
C	-5.284781000186	1.346741810919	0.877784932855
C	-4.874225710854	-0.534105476720	-0.564164331995
C	-6.620928682581	1.360676106240	0.482025968582
C	-6.209120301522	-0.524358031793	-0.962615220934
C	-7.086840674754	0.424607591180	-0.439572194604
H	-4.925500869573	2.077323920889	1.600441025989
H	-4.191820426811	-1.278991776907	-0.973097163882
H	-7.299610675500	2.100509822054	0.897043280478
H	-6.566208050793	-1.259866781951	-1.678136946397
H	-8.128618695429	0.431680574290	-0.746088061720



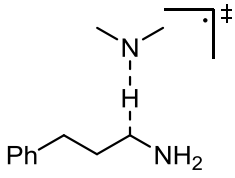
TS_HAT_61_aH

N	0.865825000000	2.463143000000	-0.521253000000
H	0.514217000000	2.740175000000	-1.429502000000
C	0.181193000000	1.517455000000	0.248575000000
H	0.852915000000	0.408330000000	0.164598000000
H	0.339693000000	1.698962000000	1.319397000000
C	-1.231145000000	1.221433000000	-0.173291000000
H	-1.236124000000	0.717845000000	-1.150547000000
H	-1.770459000000	2.167546000000	-0.325761000000
C	-1.975115000000	0.373469000000	0.858423000000
H	-2.034352000000	0.929473000000	1.801141000000
H	-1.391007000000	-0.531749000000	1.076090000000
C	2.081336000000	2.967411000000	-0.109796000000
O	2.527942000000	3.877217000000	-0.986830000000
O	2.648783000000	2.607159000000	0.904153000000
C	2.779202000000	-0.340846000000	-0.838881000000
N	1.673119000000	-0.688782000000	0.085462000000
C	0.918318000000	-1.862028000000	-0.416721000000
C	2.199929000000	-0.941413000000	1.450421000000
C	3.607526000000	-1.615291000000	-1.105643000000
H	3.366619000000	0.439200000000	-0.347557000000
H	2.341921000000	0.075750000000	-1.751248000000
C	3.251006000000	-2.649468000000	-0.034280000000
C	1.810945000000	-3.112153000000	-0.269179000000
H	1.468978000000	-3.727211000000	0.569165000000
H	1.734664000000	-3.723884000000	-1.171933000000
H	3.935257000000	-3.500097000000	-0.085820000000
C	3.333127000000	-1.982755000000	1.342463000000
H	4.671856000000	-1.367504000000	-1.080136000000
H	3.390977000000	-2.013021000000	-2.102256000000
H	-0.007375000000	-1.944213000000	0.159189000000
H	0.654652000000	-1.655669000000	-1.458179000000
H	1.361423000000	-1.296349000000	2.056764000000
H	2.539293000000	0.015545000000	1.855839000000
H	3.230301000000	-2.720462000000	2.142517000000
H	4.306566000000	-1.499461000000	1.471183000000
H	3.376485000000	4.211623000000	-0.660522000000
C	-3.354094000000	-0.010153000000	0.399485000000
C	-4.484069000000	0.644233000000	0.897546000000
C	-3.528555000000	-1.012785000000	-0.561814000000
C	-5.759730000000	0.303501000000	0.450079000000
C	-4.800660000000	-1.356367000000	-1.011444000000
C	-5.921035000000	-0.697428000000	-0.505508000000
H	-4.362387000000	1.423116000000	1.647787000000
H	-2.657627000000	-1.535417000000	-0.957292000000
H	-6.627846000000	0.818685000000	0.851635000000
H	-4.919564000000	-2.141238000000	-1.753019000000
H	-6.914550000000	-0.966409000000	-0.852208000000



TS_HAT_60_gH

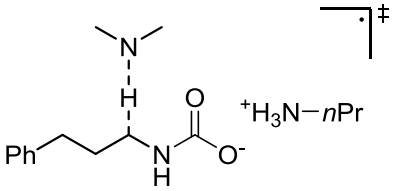
N	-2.239626000000	1.397209000000	-1.346537000000
H	-2.125578000000	1.689084000000	-2.306136000000
C	-1.173135000000	1.611560000000	-0.424120000000
H	-0.721476000000	2.593412000000	-0.606462000000
H	-1.583188000000	1.602330000000	0.588949000000
C	-0.067786000000	0.519089000000	-0.516999000000
H	0.339807000000	0.523469000000	-1.535857000000
H	-0.558726000000	-0.448050000000	-0.367315000000
C	1.001082000000	0.729497000000	0.510547000000
H	1.806724000000	-0.277062000000	0.348484000000
H	0.670050000000	0.527904000000	1.537288000000
C	1.900720000000	1.875498000000	0.431095000000
C	2.594729000000	2.298388000000	1.587346000000
C	2.174002000000	2.536481000000	-0.787116000000
C	3.515296000000	3.334127000000	1.530332000000
C	3.091929000000	3.575598000000	-0.840032000000
C	3.770111000000	3.976513000000	0.315047000000
H	2.387142000000	1.803463000000	2.534282000000
H	1.656937000000	2.230855000000	-1.693617000000
H	4.032514000000	3.650260000000	2.431150000000
H	3.283142000000	4.079483000000	-1.782716000000
H	4.489496000000	4.788424000000	0.268826000000
N	2.728024000000	-1.285634000000	0.182684000000
C	3.086988000000	-3.657029000000	-0.351730000000
C	2.066935000000	-2.499228000000	-0.349316000000
H	1.708910000000	-2.255937000000	-1.354023000000
H	1.195301000000	-2.708381000000	0.276998000000
C	4.557982000000	-2.499461000000	1.289594000000
C	3.349884000000	-1.563479000000	1.497982000000
H	3.634234000000	-0.603965000000	1.940850000000
H	2.577084000000	-2.011009000000	2.129525000000
C	4.704787000000	-1.931593000000	-1.128766000000
C	3.742612000000	-0.779910000000	-0.770497000000
H	4.252276000000	0.057155000000	-0.281550000000
H	3.215788000000	-0.384855000000	-1.644559000000
C	4.484159000000	-3.070653000000	-0.129348000000
H	3.035519000000	-4.194761000000	-1.302415000000
H	2.850612000000	-4.376620000000	0.438745000000
H	5.244250000000	-3.844350000000	-0.265291000000
H	5.495610000000	-1.951372000000	1.426921000000
H	4.540457000000	-3.299216000000	2.035056000000
H	5.738055000000	-1.575641000000	-1.095588000000
H	4.517098000000	-2.282820000000	-2.148531000000
C	-3.250297000000	0.455205000000	-1.122920000000
O	-3.282423000000	-0.095947000000	0.016380000000
O	-4.046664000000	0.270034000000	-2.094329000000
H	-5.243961000000	-0.738457000000	-1.472742000000
N	-5.638775000000	-1.199187000000	-0.604438000000
H	-5.845057000000	-2.182584000000	-0.759908000000
H	-4.791973000000	-1.083780000000	-0.002927000000
C	-6.797145000000	-0.453229000000	-0.053181000000
H	-6.487485000000	0.595037000000	-0.001998000000
H	-7.614472000000	-0.520480000000	-0.776412000000
C	-7.211747000000	-0.972619000000	1.308124000000
H	-6.356873000000	-0.907913000000	1.992676000000
H	-7.467181000000	-2.037233000000	1.230550000000
C	-8.390285000000	-0.194967000000	1.867204000000
H	-9.262948000000	-0.266700000000	1.210743000000
H	-8.148278000000	0.866118000000	1.980848000000
H	-8.683415000000	-0.573931000000	2.848321000000



TS_HAT_9_aH_NMe2

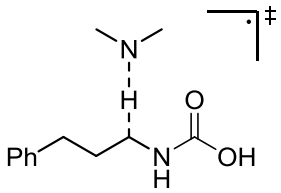
N	2.730603000000	2.269881000000	-0.905157000000
H	2.650603000000	1.915378000000	-1.852190000000
C	2.052936000000	1.450327000000	0.039800000000
H	2.675632000000	0.283977000000	0.099827000000
H	2.186441000000	1.844662000000	1.055745000000
C	0.608645000000	1.195868000000	-0.305043000000
H	0.543532000000	0.691092000000	-1.281557000000
H	0.074503000000	2.150893000000	-0.430117000000
C	-0.105990000000	0.347727000000	0.747267000000
H	-0.053968000000	0.862668000000	1.715442000000
H	0.433894000000	-0.600371000000	0.871597000000
H	3.713147000000	2.384072000000	-0.687702000000

N	3.269553000000	-0.881070000000	0.048178000000
C	2.555554000000	-1.635330000000	-0.954983000000
H	1.508871000000	-1.874424000000	-0.680471000000
H	2.545590000000	-1.088864000000	-1.904498000000
H	3.057424000000	-2.597724000000	-1.134045000000
C	3.141135000000	-1.494579000000	1.349774000000
H	3.517297000000	-0.818851000000	2.124731000000
H	2.107631000000	-1.787263000000	1.615484000000
H	3.744692000000	-2.413392000000	1.390566000000
C	-1.537243000000	0.067136000000	0.388769000000
C	-1.870270000000	-1.052385000000	-0.382397000000
C	-2.563352000000	0.936458000000	0.774751000000
C	-3.189554000000	-1.300883000000	-0.754804000000
C	-3.884982000000	0.692968000000	0.405312000000
C	-4.202667000000	-0.427833000000	-0.361032000000
H	-1.081731000000	-1.738950000000	-0.688632000000
H	-2.320281000000	1.811285000000	1.375627000000
H	-3.428020000000	-2.178844000000	-1.349243000000
H	-4.668590000000	1.377320000000	0.720100000000
H	-5.233035000000	-0.621179000000	-0.646292000000



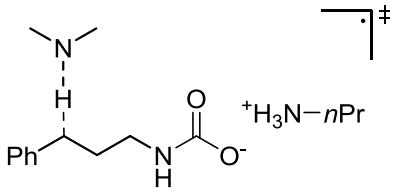
TS_HAT_60_aH_NMe2

N	-0.709216000000	-1.143205000000	-0.489385000000
H	-0.599099000000	-1.067238000000	-1.491296000000
C	0.264021000000	-0.536422000000	0.333604000000
H	-0.062334000000	0.733398000000	0.418973000000
H	0.134559000000	-0.867392000000	1.369383000000
C	1.674195000000	-0.648770000000	-0.182285000000
H	1.753320000000	-0.183624000000	-1.176993000000
H	1.943371000000	-1.706841000000	-0.328388000000
C	2.687723000000	0.003145000000	0.759535000000
H	2.608815000000	-0.467542000000	1.747846000000
H	2.421839000000	1.059495000000	0.899210000000
C	-2.025849000000	-1.348738000000	-0.065878000000
O	-2.852659000000	-1.642193000000	-1.000856000000
O	-2.282179000000	-1.249594000000	1.160753000000
H	-4.195946000000	-1.683052000000	-0.258015000000
N	-4.910864000000	-1.495898000000	0.544815000000
H	-5.638949000000	-2.203329000000	0.597421000000
H	-4.270157000000	-1.565940000000	1.346325000000
C	-5.455353000000	-0.122155000000	0.419485000000
H	-6.080000000000	0.091425000000	1.291968000000
H	-4.590676000000	0.547765000000	0.456540000000
C	-6.224367000000	0.049968000000	-0.874260000000
H	-7.058009000000	-0.664024000000	-0.903879000000
H	-5.566868000000	-0.204936000000	-1.714056000000
C	-6.748898000000	1.466609000000	-1.027157000000
H	-5.930672000000	2.193451000000	-1.031529000000
H	-7.423916000000	1.733652000000	-0.207592000000
H	-7.301323000000	1.584984000000	-1.961928000000
N	-0.386210000000	2.007376000000	0.472066000000
C	-0.053529000000	2.442988000000	1.808206000000
H	-0.409765000000	3.471539000000	1.968559000000
H	-0.548155000000	1.800990000000	2.544832000000
H	1.032263000000	2.449023000000	2.024734000000
C	0.426871000000	2.676743000000	-0.515016000000
H	1.510593000000	2.683228000000	-0.284123000000
H	0.285742000000	2.213596000000	-1.497868000000
H	0.123166000000	3.730874000000	-0.600938000000
C	4.095661000000	-0.106882000000	0.249101000000
C	4.922457000000	-1.164247000000	0.643684000000
C	4.594788000000	0.816460000000	-0.677148000000
C	6.211186000000	-1.297295000000	0.129955000000
C	5.882357000000	0.688759000000	-1.193735000000
C	6.695746000000	-0.370505000000	-0.791716000000
H	4.547620000000	-1.889996000000	1.363448000000
H	3.963059000000	1.645957000000	-0.992768000000
H	6.838368000000	-2.124909000000	0.451071000000
H	6.253027000000	1.418621000000	-1.908691000000
H	7.700801000000	-0.470734000000	-1.192129000000



TS_HAT_61_aH_NMe2

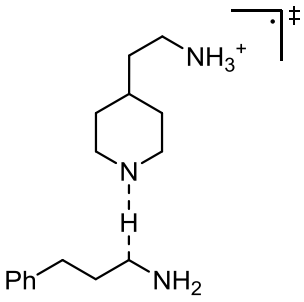
N	-2.360442000000	-1.168076000000	-0.511399000000
H	-2.160254000000	-1.358964000000	-1.483252000000
C	-1.409285000000	-0.454269000000	0.263834000000
H	-1.707424000000	0.831606000000	0.084383000000
H	-1.621002000000	-0.591695000000	1.328792000000
C	0.020230000000	-0.703120000000	-0.128481000000
H	0.182493000000	-0.405897000000	-1.175485000000
H	0.249953000000	-1.779312000000	-0.085507000000
C	0.993567000000	0.058871000000	0.771190000000
H	0.852449000000	-0.266552000000	1.809218000000
H	0.737252000000	1.126929000000	0.748687000000
C	-3.655878000000	-1.290515000000	-0.110350000000
O	-4.408066000000	-1.851794000000	-1.092151000000
O	-4.090882000000	-0.968698000000	0.983177000000
N	-1.989554000000	2.072050000000	-0.085331000000
C	-1.863977000000	2.689020000000	1.215881000000
H	-0.828377000000	2.717323000000	1.602749000000
H	-2.493827000000	2.163974000000	1.940573000000
H	-5.304041000000	-1.927799000000	-0.737345000000
H	-2.209132000000	3.730931000000	1.163830000000
C	-1.029788000000	2.609433000000	-1.021955000000
H	0.002798000000	2.674543000000	-0.630451000000
H	-1.019715000000	2.010829000000	-1.938768000000
H	-1.322019000000	3.632150000000	-1.299376000000
C	2.427878000000	-0.130267000000	0.366850000000
C	2.928491000000	0.486049000000	-0.787170000000
C	3.286142000000	-0.947572000000	1.108437000000
C	4.248312000000	0.292991000000	-1.186583000000
C	4.608745000000	-1.144043000000	0.713143000000
C	5.094254000000	-0.524271000000	-0.436319000000
H	2.274060000000	1.127925000000	-1.375914000000
H	2.911886000000	-1.431816000000	2.008739000000
H	4.619128000000	0.783394000000	-2.082918000000
H	5.260226000000	-1.780846000000	1.305567000000
H	6.124953000000	-0.674443000000	-0.745473000000



TS_HAT_60_gH_NMe2

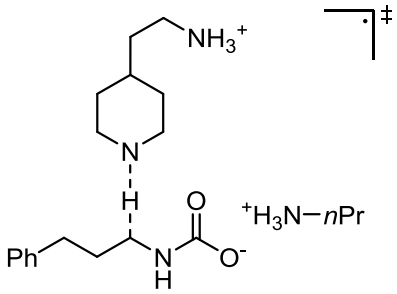
C	-0.744523000000	0.175871000000	-0.452210000000
H	-1.078510000000	0.029855000000	-1.489203000000
H	-0.055770000000	1.028062000000	-0.472999000000
C	-1.916594000000	0.493942000000	0.441973000000
H	-2.372610000000	1.609949000000	-0.036172000000
H	-1.613880000000	0.828503000000	1.442078000000
C	-3.058872000000	-0.426904000000	0.493623000000
C	-3.958346000000	-0.372175000000	1.577814000000
C	-3.355077000000	-1.324065000000	-0.551775000000
C	-5.096769000000	-1.169295000000	1.614482000000
C	-4.491198000000	-2.125284000000	-0.512309000000
C	-5.371572000000	-2.051747000000	0.568123000000
H	-3.745839000000	0.308755000000	2.400812000000
H	-2.685918000000	-1.392397000000	-1.406997000000
H	-5.770859000000	-1.107427000000	2.465030000000
H	-4.692104000000	-2.812396000000	-1.330410000000
H	-6.258861000000	-2.677625000000	0.596433000000
C	-3.763339000000	3.162672000000	0.648001000000
N	-3.039394000000	2.658420000000	-0.496065000000
H	-4.328567000000	4.060906000000	0.361923000000
H	-4.496495000000	2.441401000000	1.054420000000

H	-3.067370000000	3.442237000000	1.444564000000
C	-3.948872000000	2.095887000000	-1.467513000000
H	-4.542832000000	2.898684000000	-1.926667000000
H	-4.665709000000	1.375178000000	-1.030996000000
H	-3.390902000000	1.591411000000	-2.262245000000
N	1.150691000000	-1.395170000000	-0.863852000000
H	0.937876000000	-1.824017000000	-1.752116000000
C	0.040395000000	-1.062729000000	-0.001678000000
C	2.330604000000	-0.667322000000	-0.857004000000
H	-0.628500000000	-1.930296000000	0.052602000000
H	0.435059000000	-0.894621000000	1.004918000000
O	2.547111000000	0.099861000000	0.134217000000
O	3.116477000000	-0.861976000000	-1.844766000000
N	4.942037000000	0.655960000000	-0.786819000000
H	4.437586000000	0.062645000000	-1.515072000000
H	5.232738000000	1.555696000000	-1.159386000000
H	4.104819000000	0.752290000000	-0.150475000000
C	6.046211000000	-0.081160000000	-0.135450000000
H	5.633346000000	-1.051690000000	0.157461000000
H	6.820732000000	-0.268424000000	-0.885228000000
C	6.605218000000	0.658376000000	1.063297000000
H	5.796816000000	0.841269000000	1.781885000000
H	6.967286000000	1.645478000000	0.747455000000
C	7.729068000000	-0.119384000000	1.725113000000
H	8.555631000000	-0.294799000000	1.029004000000
H	7.382013000000	-1.095614000000	2.077786000000
H	8.130768000000	0.419332000000	2.586216000000



TS_HAT_9_aH_remoteNH3

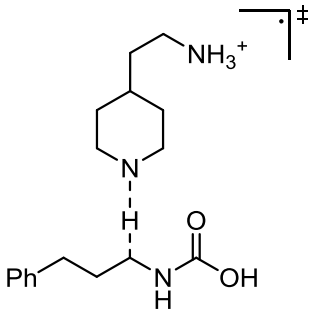
N	-1.556107000000	3.830593000000	-1.170600000000
H	-1.376984000000	3.472942000000	-2.102096000000
C	-1.479532000000	2.835037000000	-0.163633000000
H	-0.241665000000	2.433824000000	-0.061773000000
H	-1.669252000000	3.272784000000	0.825232000000
C	-2.333638000000	1.623355000000	-0.441893000000
H	-1.985522000000	1.126148000000	-1.360695000000
H	-3.368557000000	1.934329000000	-0.648889000000
C	-2.324857000000	0.619419000000	0.710975000000
H	-2.718255000000	1.107614000000	1.611696000000
H	-1.286317000000	0.343368000000	0.938340000000
H	-0.955586000000	4.626680000000	-0.997618000000
N	1.015315000000	1.983115000000	-0.049800000000
C	1.030304000000	0.812737000000	-0.903991000000
C	1.341823000000	1.598252000000	1.310813000000
C	2.947158000000	-0.123917000000	0.425757000000
C	2.442096000000	0.233385000000	-0.973912000000
H	3.114668000000	0.978084000000	-1.423199000000
H	2.439762000000	-0.643680000000	-1.634653000000
C	2.773665000000	1.071595000000	1.362789000000
H	0.349869000000	0.013511000000	-0.537838000000
H	0.686306000000	1.092603000000	-1.907261000000
H	0.669257000000	0.805908000000	1.700513000000
H	1.230542000000	2.467236000000	1.968844000000
H	3.461042000000	1.872975000000	1.057926000000
H	3.038362000000	0.791958000000	2.390411000000
H	2.320993000000	-0.946128000000	0.811386000000
C	4.401892000000	-0.592665000000	0.430575000000
H	4.711509000000	-0.789397000000	1.465927000000
H	5.043314000000	0.218125000000	0.056846000000
C	4.612865000000	-1.834670000000	-0.405232000000
H	3.981803000000	-2.665417000000	-0.081397000000
H	4.437793000000	-1.662853000000	-1.468825000000
N	6.038462000000	-2.318361000000	-0.290704000000
H	6.699375000000	-1.603727000000	-0.600873000000
H	6.206426000000	-3.154170000000	-0.852696000000
H	6.275722000000	-2.547170000000	0.676171000000
C	-3.118996000000	-0.618562000000	0.406749000000
C	-4.474568000000	-0.706930000000	0.740883000000
C	-2.527888000000	-1.696491000000	-0.262268000000
C	-5.218861000000	-1.840230000000	0.418436000000
C	-3.266731000000	-2.831871000000	-0.587441000000
C	-4.616948000000	-2.907131000000	-0.247051000000
H	-4.949102000000	0.122665000000	1.262088000000
H	-1.472172000000	-1.640583000000	-0.527765000000
H	-6.269692000000	-1.891215000000	0.690108000000
H	-2.788704000000	-3.659854000000	-1.104341000000
H	-5.195343000000	-3.791858000000	-0.497189000000



TS_HAT_60_aH_remoteNH3

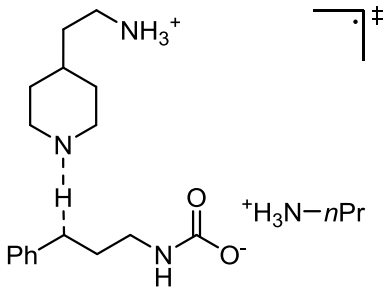
N	1.997575000000	0.635510000000	-0.735536000000
H	1.933601000000	0.862367000000	-1.718153000000
C	0.886353000000	0.876218000000	0.093832000000
H	0.118723000000	-0.164529000000	0.020079000000
H	1.195011000000	0.837449000000	1.144433000000
C	0.083068000000	2.098501000000	-0.271161000000
H	-0.324861000000	1.993985000000	-1.287995000000
H	0.735822000000	2.983773000000	-0.303398000000
C	-1.058868000000	2.348234000000	0.713796000000
H	-0.642493000000	2.476158000000	1.720760000000
H	-1.691228000000	1.450022000000	0.760652000000
C	3.034479000000	-0.240545000000	-0.393104000000
O	3.873176000000	-0.471311000000	-1.330501000000
O	3.064379000000	-0.692630000000	0.780494000000
H	4.697003000000	-1.799429000000	0.892254000000
N	5.463013000000	-1.828932000000	0.202193000000
H	5.736688000000	-2.788894000000	0.008957000000
H	4.939714000000	-1.375795000000	-0.631381000000
C	6.608807000000	-0.984128000000	0.619001000000
H	6.188942000000	-0.004032000000	0.865201000000
H	7.037191000000	-1.401616000000	1.535027000000
C	7.643994000000	-0.873909000000	-0.481717000000
H	7.164358000000	-0.475977000000	-1.384225000000
H	8.010346000000	-1.875899000000	-0.740490000000
C	8.805500000000	0.012396000000	-0.068209000000
H	9.310923000000	-0.380416000000	0.819827000000
H	8.467007000000	1.026570000000	0.165458000000
H	9.548528000000	0.087567000000	-0.864887000000
C	-1.784727000000	-0.961726000000	-0.900905000000
N	-0.668768000000	-1.249980000000	-0.025038000000
C	-1.148201000000	-1.451243000000	1.328053000000
C	-2.704606000000	-2.181598000000	-0.981035000000
H	-2.393876000000	-0.100495000000	-0.551055000000
H	-1.407130000000	-0.705722000000	-1.898245000000
C	-2.023806000000	-2.698118000000	1.376425000000
H	-1.745229000000	-0.590706000000	1.697900000000
H	-0.288658000000	-1.559873000000	1.999367000000
C	-3.204459000000	-2.572483000000	0.412033000000
H	-3.851759000000	-1.758299000000	0.779529000000
C	-4.020397000000	-3.864562000000	0.407931000000
H	-2.146904000000	-3.023651000000	-1.415546000000
H	-3.541509000000	-1.961452000000	-1.657380000000
H	-1.417217000000	-3.569656000000	1.093510000000
H	-2.384539000000	-2.872861000000	2.398203000000
H	-4.287310000000	-4.122824000000	1.441476000000
H	-3.393803000000	-4.684086000000	0.027769000000
C	-5.277582000000	-3.755957000000	-0.424044000000
H	-5.939673000000	-2.960514000000	-0.074679000000
H	-5.072244000000	-3.593926000000	-1.483834000000

N	-6.078754000000	-5.034627000000	-0.348674000000
H	-5.544727000000	-5.828893000000	-0.706454000000
H	-6.942350000000	-4.978159000000	-0.890285000000
H	-6.336590000000	-5.255991000000	0.614890000000
C	-1.900429000000	3.541034000000	0.358856000000
C	-1.881941000000	4.697746000000	1.144007000000
C	-2.711490000000	3.527262000000	-0.783536000000
C	-2.651518000000	5.809762000000	0.803538000000
C	-3.481106000000	4.635189000000	-1.129017000000
C	-3.454042000000	5.782086000000	-0.334946000000
H	-1.256645000000	4.723877000000	2.034451000000
H	-2.738605000000	2.635122000000	-1.408480000000
H	-2.623523000000	6.697906000000	1.428922000000
H	-4.104562000000	4.604999000000	-2.018721000000
H	-4.054512000000	6.646682000000	-0.602813000000



TS_HAT_61_aH_remoteNH3

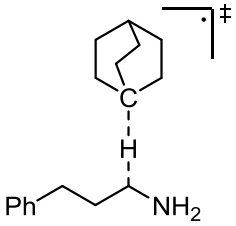
N	-1.570728000000	3.076642000000	-0.630729000000
H	-1.881327000000	2.992566000000	-1.588521000000
C	-1.436451000000	1.913317000000	0.166790000000
H	-0.191726000000	1.521923000000	0.020961000000
H	-1.456591000000	2.186938000000	1.227045000000
C	-2.363111000000	0.789402000000	-0.206853000000
H	-2.150233000000	0.448994000000	-1.231223000000
H	-3.405388000000	1.142188000000	-0.220151000000
C	-2.237564000000	-0.386263000000	0.761899000000
H	-2.509264000000	-0.050244000000	1.769958000000
H	-1.182393000000	-0.689194000000	0.817234000000
C	-1.012647000000	4.262149000000	-0.254203000000
O	-1.152663000000	5.185402000000	-1.236656000000
O	-0.477692000000	4.476234000000	0.820631000000
H	-0.765230000000	6.005835000000	-0.902389000000
N	1.061291000000	1.159975000000	-0.059041000000
C	1.154957000000	-0.057594000000	-0.839905000000
C	1.481588000000	0.903612000000	1.306830000000
C	2.623183000000	-0.467967000000	-0.954230000000
H	0.598343000000	-0.901826000000	-0.383250000000
H	0.728433000000	0.114205000000	-1.834835000000
C	2.963155000000	0.540625000000	1.315758000000
H	0.911513000000	0.072663000000	1.771118000000
H	1.300750000000	1.800704000000	1.908788000000
C	3.234040000000	-0.679009000000	0.433681000000
H	2.733685000000	-1.546842000000	0.894964000000
C	4.735129000000	-0.964484000000	0.384793000000
H	3.176568000000	0.323001000000	-1.480086000000
H	2.695520000000	-1.377282000000	-1.564737000000
H	3.540059000000	1.395770000000	0.937823000000
H	3.299410000000	0.352972000000	2.342839000000
H	5.114297000000	-1.061456000000	1.410993000000
H	5.249956000000	-0.102576000000	-0.062757000000
C	5.071691000000	-2.215801000000	-0.393927000000
H	4.586464000000	-3.104956000000	0.015052000000
H	4.816675000000	-2.138362000000	-1.452160000000
N	6.556873000000	-2.484754000000	-0.345359000000
H	7.087394000000	-1.709159000000	-0.746789000000
H	6.811309000000	-3.327900000000	-0.862186000000
H	6.881924000000	-2.604816000000	0.615948000000
C	-3.082795000000	-1.565807000000	0.372179000000
C	-4.223857000000	-1.909450000000	1.102823000000
C	-2.753722000000	-2.335633000000	-0.750796000000
C	-5.014891000000	-2.994690000000	0.727332000000
C	-3.540744000000	-3.419637000000	-1.130802000000
C	-4.675548000000	-3.753206000000	-0.390938000000
H	-4.492197000000	-1.320318000000	1.977659000000
H	-1.867277000000	-2.081960000000	-1.331682000000
H	-5.896418000000	-3.247578000000	1.309926000000
H	-3.268439000000	-4.006986000000	-2.003602000000
H	-5.289506000000	-4.599817000000	-0.684420000000



TS_HAT_60_gH_remoteNH3

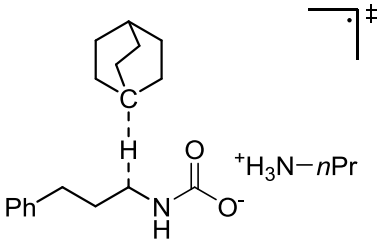
C	0.905948000000	0.366688000000	0.367217000000
H	0.402445000000	0.165708000000	1.323381000000
H	1.290272000000	-0.596494000000	0.011777000000
C	-0.061582000000	0.930952000000	-0.643432000000
H	-0.932659000000	-0.002079000000	-0.809494000000
H	0.364083000000	0.976179000000	-1.653337000000
C	-0.815021000000	2.149060000000	-0.315667000000
C	-1.263673000000	2.997705000000	-1.346629000000
C	-1.183107000000	2.474866000000	1.004765000000
C	-2.039961000000	4.117681000000	-1.074673000000
C	-1.961643000000	3.595825000000	1.277234000000
C	-2.395691000000	4.423144000000	0.240955000000
H	-0.988546000000	2.763006000000	-2.373599000000
H	-0.846844000000	1.846338000000	1.826934000000
H	-2.364303000000	4.760225000000	-1.889075000000
H	-2.224715000000	3.830236000000	2.305394000000
H	-2.997328000000	5.301399000000	0.456839000000
C	-3.077563000000	-0.082758000000	-1.320528000000
N	-1.967094000000	-0.858023000000	-0.798108000000
C	-4.361200000000	-0.910155000000	-1.272663000000
H	-3.239029000000	0.847378000000	-0.737558000000
H	-2.852835000000	0.216492000000	-2.350234000000
C	-2.194477000000	-1.139093000000	0.608793000000
C	-3.431562000000	-2.019123000000	0.765169000000
H	-2.345025000000	-0.205617000000	1.190464000000
H	-1.314609000000	-1.644408000000	1.020922000000
C	-4.664236000000	-1.349245000000	0.160235000000
H	-4.243164000000	-1.798964000000	-1.908918000000
H	-5.182848000000	-0.316670000000	-1.693632000000
H	-3.253517000000	-2.976383000000	0.255539000000
H	-3.598578000000	-2.245615000000	1.825328000000
H	-4.883230000000	-0.445759000000	0.753220000000
C	-5.868839000000	-2.285635000000	0.252789000000
H	-5.992185000000	-2.608059000000	1.295546000000
H	-5.666300000000	-3.190893000000	-0.336847000000
C	-7.148047000000	-1.640073000000	-0.228432000000
H	-7.387489000000	-0.728873000000	0.324451000000
H	-7.129581000000	-1.402378000000	-1.293544000000
N	-8.319638000000	-2.572769000000	-0.031148000000
H	-8.190000000000	-3.446454000000	-0.544948000000
H	-9.196791000000	-2.158466000000	-0.350085000000
H	-8.437688000000	-2.817770000000	0.953800000000
H	2.873011000000	0.767427000000	2.518806000000
N	3.079603000000	0.750965000000	1.531729000000
C	2.102218000000	1.295019000000	0.622237000000
C	3.978406000000	-0.233345000000	1.145872000000
H	1.748014000000	2.254604000000	1.018341000000
H	2.604709000000	1.501058000000	-0.327775000000
O	4.097281000000	-0.454688000000	-0.104541000000
O	4.628836000000	-0.805394000000	2.077298000000
H	5.792510000000	-1.809024000000	1.271937000000
N	6.162181000000	-1.997041000000	0.304205000000
H	6.212663000000	-2.991859000000	0.103052000000
H	5.355302000000	-1.526421000000	-0.206184000000
C	7.438391000000	-1.291663000000	0.046902000000
H	7.291145000000	-0.262627000000	0.389627000000
H	8.214343000000	-1.739412000000	0.674715000000
C	7.818072000000	-1.328438000000	-1.419601000000
H	7.003000000000	-0.890854000000	-2.009381000000
H	7.911973000000	-2.372025000000	-1.747227000000

C	9.114781000000	-0.583241000000	-1.681800000000
H	9.946873000000	-1.020421000000	-1.120661000000
H	9.034895000000	0.467995000000	-1.388106000000
H	9.380451000000	-0.610845000000	-2.740725000000



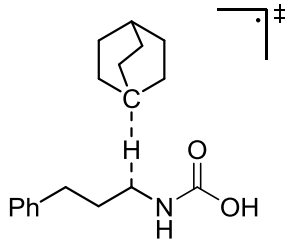
TS_HAT_9_aH_BiCyOct

N	0.628509000000	3.287365000000	-0.849275000000
H	0.718050000000	2.901194000000	-1.784258000000
C	0.206937000000	2.286788000000	0.085944000000
H	1.080923000000	1.285676000000	0.145632000000
H	0.211303000000	2.694355000000	1.104953000000
C	-1.110259000000	1.652454000000	-0.276207000000
H	-1.033575000000	1.191803000000	-1.273954000000
H	-1.895652000000	2.419736000000	-0.364040000000
C	-1.545356000000	0.590590000000	0.734208000000
H	-1.616281000000	1.051690000000	1.728019000000
H	-0.763115000000	-0.176915000000	0.805068000000
H	1.528010000000	3.679990000000	-0.595851000000
C	3.372292000000	0.950634000000	-0.179174000000
C	2.048875000000	0.271112000000	0.108054000000
C	1.713781000000	-0.709912000000	-0.996007000000
C	2.096551000000	-0.439659000000	1.444448000000
C	4.450197000000	-0.145684000000	-0.403487000000
H	3.649235000000	1.599944000000	0.662608000000
H	3.294028000000	1.597863000000	-1.062718000000
C	3.876102000000	-1.502454000000	0.021676000000
C	2.733656000000	-1.882642000000	-0.927282000000
H	2.246002000000	-2.796015000000	-0.563112000000
H	3.128839000000	-2.115254000000	-1.923444000000
H	4.660675000000	-2.267727000000	-0.016306000000
C	3.329779000000	-1.385109000000	1.449559000000
H	5.359950000000	0.078243000000	0.166571000000
H	4.745587000000	-0.187482000000	-1.459707000000
H	0.687994000000	-1.088648000000	-0.889303000000
H	1.763407000000	-0.208554000000	-1.972736000000
H	1.173527000000	-1.016393000000	1.593953000000
H	2.153271000000	0.279771000000	2.271970000000
H	3.060679000000	-2.374412000000	1.838749000000
H	4.115483000000	-0.993113000000	2.108269000000
C	-2.854415000000	-0.050177000000	0.372925000000
C	-2.898195000000	-1.132220000000	-0.514107000000
C	-4.062931000000	0.446894000000	0.872915000000
C	-4.112138000000	-1.702406000000	-0.890814000000
C	-5.280477000000	-0.119993000000	0.500543000000
C	-5.309147000000	-1.197307000000	-0.383692000000
H	-1.965052000000	-1.531459000000	-0.909645000000
H	-4.045181000000	1.288387000000	1.563771000000
H	-4.124097000000	-2.545576000000	-1.576655000000
H	-6.207955000000	0.278242000000	0.903568000000
H	-6.257134000000	-1.642341000000	-0.673483000000



TS_HAT_60_aH_BiCyOct

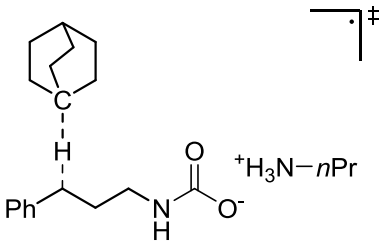
N	-1.024912000000	-0.811686000000	-0.636955000000
H	-0.881302000000	-0.836989000000	-1.636654000000
C	0.105313000000	-0.598662000000	0.193511000000
H	0.431358000000	0.679461000000	0.156313000000
H	-0.179367000000	-0.745827000000	1.239441000000
C	1.332820000000	-1.367100000000	-0.219296000000
H	1.610582000000	-1.108195000000	-1.253240000000
H	1.128286000000	-2.449500000000	-0.227610000000
C	2.517733000000	-1.082583000000	0.704927000000
H	2.225179000000	-1.306498000000	1.738770000000
H	2.740442000000	-0.007166000000	0.676117000000
C	-2.320095000000	-0.489490000000	-0.247440000000
O	-3.191237000000	-0.495606000000	-1.193249000000
O	-2.544535000000	-0.247765000000	0.968956000000
C	-0.607230000000	2.716340000000	-0.358250000000
C	0.685606000000	2.058079000000	0.077317000000
C	1.782377000000	2.340235000000	-0.927521000000
C	1.086706000000	2.541256000000	1.453408000000
C	-0.318339000000	4.221709000000	-0.614397000000
H	-1.367825000000	2.593074000000	0.423286000000
H	-1.007161000000	2.237281000000	-1.261725000000
C	1.054482000000	4.573463000000	-0.026693000000
C	2.139734000000	3.851152000000	-0.834766000000
H	3.112037000000	3.986779000000	-0.343544000000
H	2.229714000000	4.293096000000	-1.834494000000
H	1.215061000000	5.657594000000	-0.070671000000
C	1.112176000000	4.093965000000	1.429894000000
H	-1.097751000000	4.850677000000	-0.166893000000
H	-0.319968000000	4.439132000000	-1.690490000000
H	2.671433000000	1.724672000000	-0.733583000000
H	1.438014000000	2.085205000000	-1.939357000000
H	2.076529000000	2.143344000000	1.717279000000
H	0.385781000000	2.173285000000	2.214232000000
H	2.014166000000	4.477659000000	1.922080000000
H	0.256165000000	4.503041000000	1.982195000000
H	-4.484962000000	0.127476000000	1.104243000000
N	-5.182330000000	-0.099104000000	0.380070000000
H	-5.840627000000	0.665643000000	0.257992000000
H	-4.491009000000	-0.205651000000	-0.465356000000
C	-5.852679000000	-1.388833000000	0.663727000000
H	-5.051528000000	-2.111970000000	0.845480000000
H	-6.429717000000	-1.293729000000	1.588780000000
C	-6.727320000000	-1.825288000000	-0.494158000000
H	-6.114611000000	-1.881429000000	-1.401930000000
H	-7.492295000000	-1.060901000000	-0.682926000000
C	-7.387986000000	-3.165011000000	-0.221848000000
H	-8.020921000000	-3.124972000000	0.670513000000
H	-6.641805000000	-3.949504000000	-0.062251000000
H	-8.017236000000	-3.473448000000	-1.059520000000
C	3.741640000000	-1.873727000000	0.342954000000
C	4.527613000000	-1.515199000000	-0.759535000000
C	4.101561000000	-3.012241000000	1.071237000000
C	5.640295000000	-2.270935000000	-1.121935000000
C	5.214740000000	-3.771712000000	0.714197000000
C	5.987946000000	-3.403516000000	-0.385265000000
H	4.262245000000	-0.630436000000	-1.336894000000
H	3.500196000000	-3.302573000000	1.930961000000
H	6.239298000000	-1.974454000000	-1.979047000000
H	5.478956000000	-4.650796000000	1.296114000000
H	6.856950000000	-3.992280000000	-0.665493000000



TS_HAT_61_aH_BiCyOct

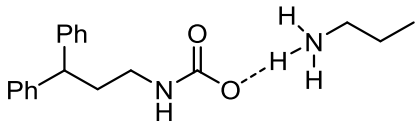
N	0.911000000000	2.484434000000	-0.509864000000
H	0.691583000000	2.499503000000	-1.495821000000
C	0.206867000000	1.579153000000	0.336887000000
H	0.861878000000	0.415595000000	0.301628000000
H	0.304892000000	1.895376000000	1.379278000000
C	-1.202117000000	1.302271000000	-0.106744000000
H	-1.191948000000	0.812611000000	-1.093103000000
H	-1.765623000000	2.238901000000	-0.241568000000

C	-1.939200000000	0.407702000000	0.890499000000
H	-2.016405000000	0.932382000000	1.850703000000
H	-1.332838000000	-0.488815000000	1.076671000000
C	2.096140000000	3.029762000000	-0.137114000000
O	2.679925000000	3.674264000000	-1.184547000000
O	2.585607000000	2.974362000000	0.981589000000
C	2.811917000000	-0.331202000000	-0.725606000000
C	1.646929000000	-0.715552000000	0.162279000000
C	0.848853000000	-1.839101000000	-0.465885000000
C	2.135069000000	-1.111814000000	1.538639000000
C	3.632097000000	-1.616939000000	-1.025608000000
H	3.436762000000	0.413672000000	-0.216614000000
H	2.461800000000	0.130262000000	-1.658539000000
C	3.170182000000	-2.734784000000	-0.083150000000
C	1.730032000000	-3.120454000000	-0.441114000000
H	1.347172000000	-3.835082000000	0.298313000000
H	1.701693000000	-3.628824000000	-1.412184000000
H	3.826763000000	-3.606769000000	-0.187468000000
C	3.209148000000	-2.220173000000	1.361641000000
H	4.704887000000	-1.429085000000	-0.900270000000
H	3.487999000000	-1.933643000000	-2.066502000000
H	-0.088158000000	-2.014036000000	0.078535000000
H	0.572185000000	-1.577189000000	-1.496303000000
H	1.294144000000	-1.479286000000	2.142034000000
H	2.551164000000	-0.245027000000	2.066939000000
H	3.036648000000	-3.043855000000	2.064257000000
H	4.209200000000	-1.825295000000	1.581067000000
H	3.499600000000	4.055537000000	-0.842751000000
C	-3.305932000000	0.010275000000	0.411340000000
C	-4.447539000000	0.697101000000	0.836691000000
C	-3.461457000000	-1.033192000000	-0.509494000000
C	-5.711299000000	0.350730000000	0.360848000000
C	-4.721746000000	-1.383777000000	-0.987672000000
C	-5.852239000000	-0.691240000000	-0.553840000000
H	-4.341488000000	1.509838000000	1.553283000000
H	-2.581260000000	-1.578131000000	-0.848955000000
H	-6.586716000000	0.894423000000	0.706256000000
H	-4.823080000000	-2.200370000000	-1.697755000000
H	-6.836341000000	-0.965345000000	-0.924008000000



TS_HAT_60_gH_BiCyOct

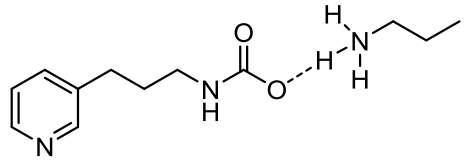
N	-2.212158000000	1.608071000000	-1.204508000000
H	-2.044493000000	1.874287000000	-2.162935000000
C	-1.117025000000	1.738229000000	-0.268899000000
H	-0.643828000000	2.714810000000	-0.427638000000
H	-1.536404000000	1.746375000000	0.742257000000
C	-0.071788000000	0.624686000000	-0.370287000000
H	0.322790000000	0.588758000000	-1.396434000000
H	-0.579551000000	-0.333806000000	-0.208577000000
C	1.055633000000	0.774780000000	0.623254000000
H	1.781338000000	-0.269179000000	0.462146000000
H	0.723768000000	0.638757000000	1.660010000000
C	1.982893000000	1.910608000000	0.490483000000
C	2.769260000000	2.308714000000	1.589237000000
C	2.200797000000	2.568730000000	-0.734971000000
C	3.731028000000	3.305179000000	1.469390000000
C	3.161549000000	3.568188000000	-0.855320000000
C	3.936735000000	3.941894000000	0.243277000000
H	2.616534000000	1.815470000000	2.548382000000
H	1.613307000000	2.288649000000	-1.606793000000
H	4.322320000000	3.590076000000	2.336043000000
H	3.306578000000	4.059767000000	-1.814259000000
H	4.686848000000	4.721725000000	0.147022000000
C	2.660022000000	-1.370179000000	0.212411000000
C	2.868864000000	-3.765266000000	-0.359287000000
C	1.873451000000	-2.572501000000	-0.251073000000
H	1.408934000000	-2.366519000000	-1.223764000000
H	1.060721000000	-2.808001000000	0.447093000000
C	4.528579000000	-2.682261000000	1.161750000000
C	3.401061000000	-1.662199000000	1.495299000000
H	3.823298000000	-0.743118000000	1.920376000000
H	2.712907000000	-2.074885000000	2.244040000000
C	4.498859000000	-2.104965000000	-1.268570000000
C	3.610343000000	-0.894541000000	-0.861349000000
H	4.223962000000	-0.066823000000	-0.481169000000
H	3.060083000000	-0.505921000000	-1.727848000000
C	4.303872000000	-3.235653000000	-0.250883000000
H	2.729910000000	-4.299042000000	-1.306789000000
H	2.685627000000	-4.493302000000	0.441163000000
H	5.015929000000	-4.045222000000	-0.451141000000
H	5.512059000000	-2.198555000000	1.213446000000
H	4.541026000000	-3.498189000000	1.894021000000
H	5.553980000000	-1.811676000000	-1.315564000000
H	4.226867000000	-2.462823000000	-2.269614000000
C	-3.208932000000	0.660818000000	-1.043542000000
O	-3.310009000000	0.100583000000	0.097201000000
O	-3.965018000000	0.454526000000	-2.050398000000
H	-5.116591000000	-0.638235000000	-1.509956000000
N	-5.488405000000	-1.128195000000	-0.645276000000
H	-5.584095000000	-2.130120000000	-0.784088000000
H	-4.648608000000	-0.889807000000	-0.040188000000
C	-6.722678000000	-0.497438000000	-0.129710000000
H	-6.523327000000	0.578346000000	-0.095869000000
H	-7.523541000000	-0.659400000000	-0.857513000000
C	-7.103631000000	-1.024004000000	1.239368000000
H	-6.269577000000	-0.856473000000	1.931911000000
H	-7.246894000000	-2.111084000000	1.185417000000
C	-8.363555000000	-0.359536000000	1.765132000000
H	-9.214219000000	-0.533074000000	1.098169000000
H	-8.232380000000	0.723086000000	1.857256000000
H	-8.633142000000	-0.744556000000	2.751175000000



45A

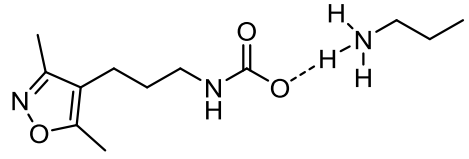
N	1.270315000000	-1.686803000000	-0.224947000000
H	1.113186000000	-2.666988000000	-0.041527000000
C	0.322664000000	-0.747248000000	0.330247000000
H	0.427393000000	-0.654315000000	1.426088000000
H	0.562145000000	0.236639000000	-0.082438000000
C	-1.105397000000	-1.145002000000	-0.002812000000
H	-1.298630000000	-2.165405000000	0.354557000000
H	-1.233810000000	-1.186655000000	-1.092782000000
C	-2.151134000000	-0.219422000000	0.628000000000
H	-1.985800000000	-0.232204000000	1.715249000000
C	-3.553256000000	-0.750691000000	0.394443000000
C	-4.337272000000	-1.189483000000	1.464636000000
C	-4.088627000000	-0.819125000000	-0.897156000000
C	-5.622833000000	-1.688198000000	1.254647000000
C	-5.369929000000	-1.318303000000	-1.112318000000
C	-6.143220000000	-1.754674000000	-0.035608000000
H	-3.932876000000	-1.136928000000	2.474360000000
H	-3.496268000000	-0.470727000000	-1.741995000000
H	-6.217323000000	-2.022295000000	2.100910000000
H	-5.768699000000	-1.364638000000	-2.122375000000
H	-7.144481000000	-2.141894000000	-0.203010000000
C	2.597748000000	-1.363935000000	-0.454728000000
O	2.918096000000	-0.130480000000	-0.440761000000
O	3.382735000000	-2.340255000000	-0.692761000000
H	4.880263000000	-1.628011000000	-1.028420000000
N	5.396095000000	-0.703651000000	-1.005766000000
H	5.846686000000	-0.498191000000	-1.893118000000
H	4.520306000000	-0.116512000000	-0.861180000000
C	6.317849000000	-0.596331000000	0.145529000000
H	5.749373000000	-0.921201000000	1.022737000000
H	7.135646000000	-1.309003000000	0.002371000000
C	6.838008000000	0.815664000000	0.326356000000
H	5.987048000000	1.496378000000	0.451534000000
H	7.356261000000	1.133746000000	-0.587727000000
C	7.774027000000	0.920451000000	1.517385000000

H	8.642482000000	0.264159000000	1.400748000000
H	7.268209000000	0.636493000000	2.445628000000
H	8.145126000000	1.940156000000	1.642173000000
C	-2.047849000000	1.229404000000	0.185977000000
C	-2.454556000000	2.241282000000	1.063228000000
C	-1.604155000000	1.597889000000	-1.088172000000
C	-2.424047000000	3.580175000000	0.682422000000
C	-1.572429000000	2.936901000000	-1.475207000000
C	-1.982739000000	3.933526000000	-0.592180000000
H	-2.801110000000	1.968113000000	2.059189000000
H	-1.267516000000	0.834688000000	-1.786974000000
H	-2.742236000000	4.348515000000	1.382288000000
H	-1.219532000000	3.200687000000	-2.468819000000
H	-1.954468000000	4.977167000000	-0.892429000000



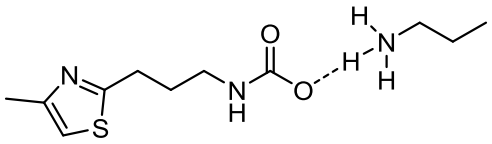
49A

N	-0.574902000000	-0.851030000000	-0.652690000000
H	-0.379514000000	-1.479491000000	-1.417645000000
C	0.306765000000	0.277446000000	-0.468557000000
H	0.245692000000	0.983752000000	-1.315060000000
H	-0.050790000000	0.818899000000	0.412138000000
C	1.750379000000	-0.158504000000	-0.281586000000
H	2.074652000000	-0.759251000000	-1.143225000000
H	1.821339000000	-0.818986000000	0.592423000000
C	2.697256000000	1.030020000000	-0.116250000000
H	2.609170000000	1.687198000000	-0.991078000000
C	4.125923000000	0.608439000000	0.051536000000
C	5.009406000000	0.598700000000	-1.032584000000
C	4.628026000000	0.163182000000	1.277047000000
N	6.283998000000	0.196800000000	-0.975563000000
C	5.949731000000	-0.259572000000	1.361762000000
C	6.735156000000	-0.226472000000	0.211342000000
H	4.660237000000	0.942548000000	-2.007999000000
H	3.985443000000	0.152734000000	2.155676000000
H	6.368011000000	-0.607601000000	2.301562000000
H	7.774270000000	-0.549948000000	0.241659000000
C	-1.890153000000	-0.872961000000	-0.221945000000
O	-2.271836000000	0.034133000000	0.585237000000
O	-2.605202000000	-1.835505000000	-0.661314000000
H	-4.079602000000	-1.639503000000	0.068262000000
N	-4.681784000000	-0.985942000000	0.654345000000
H	-5.106990000000	-1.460943000000	1.445675000000
H	-3.877423000000	-0.366566000000	0.953245000000
C	-5.662009000000	-0.241206000000	-0.165276000000
H	-5.105384000000	0.154264000000	-1.020722000000
H	-6.397058000000	-0.952579000000	-0.553667000000
C	-6.328972000000	0.875075000000	0.612720000000
H	-5.557685000000	1.552047000000	1.000502000000
H	-6.840405000000	0.455026000000	1.488566000000
C	-7.317008000000	1.643273000000	-0.247244000000
H	-8.105868000000	0.987982000000	-0.630656000000
H	-6.820896000000	2.100546000000	-1.109149000000
H	-7.798612000000	2.443450000000	0.319026000000
H	2.379536000000	1.624081000000	0.750640000000



51A

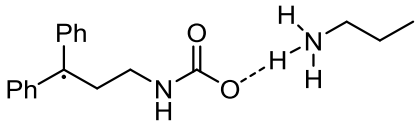
C	1.490563000000	0.000078000000	0.382146000000
H	1.761185000000	-0.623980000000	1.245883000000
H	1.644217000000	1.039578000000	0.700602000000
C	2.419796000000	-0.322871000000	-0.788074000000
H	2.151788000000	0.314156000000	-1.641614000000
N	5.976070000000	-0.641962000000	0.238032000000
C	4.772581000000	-1.137759000000	0.025886000000
O	5.883397000000	0.715209000000	-0.112054000000
C	4.623680000000	0.980702000000	-0.523500000000
C	3.866070000000	-0.154427000000	-0.465090000000
C	4.501741000000	-2.574663000000	0.287233000000
H	5.405366000000	-3.079806000000	0.632200000000
H	3.724657000000	-2.699793000000	1.047786000000
H	4.148593000000	-3.078112000000	-0.618299000000
C	4.327424000000	2.370414000000	-0.925975000000
H	3.319436000000	2.434153000000	-1.341296000000
H	4.384328000000	3.053703000000	-0.072746000000
H	5.035447000000	2.728368000000	-1.678581000000
H	2.237375000000	-1.353751000000	-1.120261000000
H	-0.628144000000	-0.318694000000	2.021610000000
N	-0.844179000000	0.101331000000	1.129197000000
C	0.031174000000	-0.211995000000	0.022430000000
C	-2.190180000000	0.383795000000	0.954999000000
H	-0.111205000000	-1.248463000000	-0.332772000000
H	-0.256245000000	0.436196000000	-0.811001000000
O	-2.585424000000	0.663875000000	-0.225143000000
O	-2.913089000000	0.367122000000	2.003348000000
H	-4.488232000000	0.817959000000	1.477248000000
N	-5.036480000000	0.975604000000	0.590318000000
H	-5.544333000000	1.855649000000	0.607192000000
H	-4.179747000000	1.017637000000	-0.043781000000
C	-5.894984000000	-0.180179000000	0.250702000000
H	-5.261018000000	-1.067296000000	0.346572000000
H	-6.686173000000	-0.258985000000	1.002282000000
C	-6.466770000000	-0.068200000000	-1.148239000000
H	-5.641350000000	0.032670000000	-1.863691000000
H	-7.059212000000	0.852533000000	-1.227805000000
C	-7.324236000000	-1.270201000000	-1.502264000000
H	-8.166061000000	-1.377759000000	-0.810668000000
H	-6.743893000000	-2.197252000000	-1.461999000000
H	-7.734876000000	-1.181334000000	-2.510419000000



52A

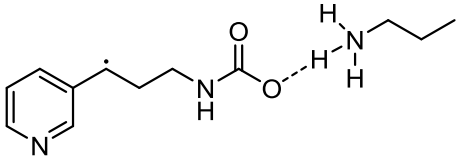
C	1.319973000000	0.271786000000	0.010232000000
H	1.655058000000	1.266261000000	0.334154000000
H	1.406082000000	0.256406000000	-1.083386000000
C	2.241425000000	-0.783487000000	0.624528000000
H	1.939134000000	-1.779434000000	0.279880000000
H	2.133613000000	-0.775138000000	1.715090000000
H	-0.770494000000	2.031191000000	0.046269000000
N	-0.993542000000	1.066963000000	-0.151342000000
C	-0.129975000000	0.053836000000	0.408452000000
C	-2.327434000000	0.845744000000	-0.450961000000
H	-0.204013000000	0.016277000000	1.509540000000
H	-0.492530000000	-0.910685000000	0.041494000000
O	-2.736683000000	-0.362125000000	-0.481220000000
O	-3.027737000000	1.880304000000	-0.701018000000
H	-4.582189000000	1.286668000000	-1.107095000000
N	-5.150173000000	0.396918000000	-1.088710000000
H	-5.613099000000	0.220182000000	-1.975801000000
H	-4.311800000000	-0.244764000000	-0.939046000000
C	-6.075143000000	0.348710000000	0.064563000000
H	-5.487402000000	0.648257000000	0.938023000000
H	-6.852941000000	1.104027000000	-0.082229000000
C	-6.670466000000	-1.031510000000	0.257242000000
H	-5.856861000000	-1.756348000000	0.383170000000
H	-7.210256000000	-1.327565000000	-0.651697000000
C	-7.603774000000	-1.076457000000	1.454236000000
H	-8.436578000000	-0.375669000000	1.336741000000
H	-7.077758000000	-0.811698000000	2.376900000000
H	-8.027823000000	-2.073698000000	1.590222000000
C	5.728386000000	0.300011000000	0.475294000000
N	4.475475000000	0.194558000000	1.038124000000
C	5.884077000000	-0.371474000000	-0.707800000000
C	6.775397000000	1.099019000000	1.169749000000
C	3.678741000000	-0.543197000000	0.312026000000
S	4.421816000000	-1.168847000000	-1.143656000000

H	6.768797000000	-0.441073000000	-1.326270000000
H	7.714628000000	1.093186000000	0.613283000000
H	6.455890000000	2.138529000000	1.293022000000
H	6.967298000000	0.704240000000	2.172266000000



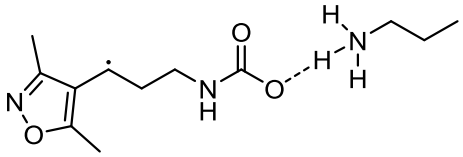
45A-gR

N	1.256766000000	-0.981738000000	-1.459284000000
H	1.136363000000	-1.873820000000	-1.916588000000
C	0.189326000000	-0.529029000000	-0.598039000000
H	0.124649000000	-1.121450000000	0.331614000000
H	0.426653000000	0.493935000000	-0.293299000000
C	-1.158790000000	-0.572646000000	-1.318641000000
H	-1.371426000000	-1.597328000000	-1.642748000000
H	-1.068087000000	0.010777000000	-2.244260000000
C	-2.293724000000	-0.053941000000	-0.482146000000
C	-2.349780000000	1.362560000000	-0.194476000000
C	-3.033506000000	1.879736000000	0.936142000000
C	-1.654733000000	2.302565000000	-0.997794000000
C	-3.048961000000	3.237946000000	1.217771000000
C	-1.679272000000	3.660659000000	-0.714973000000
C	-2.381925000000	4.144413000000	0.390259000000
H	-3.520691000000	1.192695000000	1.621308000000
H	-1.099459000000	1.961335000000	-1.866598000000
H	-3.574414000000	3.592767000000	2.100727000000
H	-1.143934000000	4.349555000000	-1.363196000000
H	-2.396991000000	5.207621000000	0.612183000000
C	2.583356000000	-0.634228000000	-1.250717000000
O	2.822113000000	0.334576000000	-0.457690000000
O	3.450221000000	-1.304325000000	-1.900284000000
H	4.961002000000	-0.618864000000	-1.470487000000
N	5.389527000000	0.065616000000	-0.790473000000
H	5.991858000000	0.738396000000	-1.256456000000
H	4.461359000000	0.498262000000	-0.494935000000
C	6.052690000000	-0.613371000000	0.344057000000
H	5.344735000000	-1.367244000000	0.702740000000
H	6.932087000000	-1.142922000000	-0.034688000000
C	6.421956000000	0.355655000000	1.449266000000
H	5.517019000000	0.877145000000	1.784701000000
H	7.093094000000	1.127050000000	1.049892000000
C	7.082507000000	-0.353583000000	2.618206000000
H	8.000553000000	-0.863447000000	2.308586000000
H	6.417100000000	-1.106540000000	3.051805000000
H	7.346281000000	0.349776000000	3.411099000000
C	-3.264515000000	-0.997149000000	0.037644000000
C	-4.616736000000	-0.642826000000	0.263287000000
C	-2.905308000000	-2.343078000000	0.290891000000
C	-5.540566000000	-1.569430000000	0.726473000000
C	-3.829566000000	-3.263237000000	0.767079000000
C	-5.154787000000	-2.885461000000	0.991117000000
H	-4.944551000000	0.366245000000	0.029182000000
H	-1.875707000000	-2.658632000000	0.140437000000
H	-6.574496000000	-1.266719000000	0.870960000000
H	-3.513664000000	-4.283429000000	0.969118000000
H	-5.878042000000	-3.607653000000	1.358540000000



49A-gR

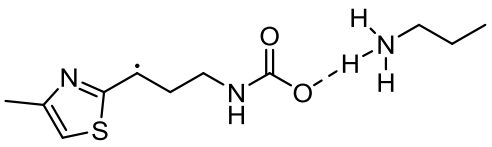
N	-0.458648000000	-1.344407000000	-0.633197000000
H	-0.222614000000	-2.320393000000	-0.729400000000
C	0.618304000000	-0.388655000000	-0.587208000000
H	1.343658000000	-0.639271000000	-1.370155000000
H	0.209948000000	0.597394000000	-0.824863000000
C	1.338851000000	-0.318862000000	0.778898000000
H	1.738836000000	-1.315546000000	1.009696000000
H	0.581748000000	-0.092616000000	1.536995000000
C	2.411637000000	0.704757000000	0.795987000000
H	2.150914000000	1.718955000000	1.099758000000
C	3.730691000000	0.494636000000	0.338489000000
C	4.669230000000	1.566286000000	0.339972000000
C	4.216445000000	-0.748627000000	-0.144894000000
N	5.926886000000	1.480566000000	-0.069700000000
C	5.528101000000	-0.845027000000	-0.574605000000
C	6.349303000000	0.284990000000	-0.523380000000
H	4.342820000000	2.542965000000	0.702572000000
H	3.560160000000	-1.615161000000	-0.178350000000
H	5.922029000000	-1.784851000000	-0.950462000000
H	7.384010000000	0.236594000000	-0.856284000000
C	-1.684715000000	-1.107068000000	-0.028884000000
O	-1.929483000000	0.086716000000	0.345575000000
O	-2.470682000000	-2.103566000000	0.067886000000
H	-3.927284000000	-1.465859000000	0.707519000000
N	-4.389758000000	-0.546037000000	0.939879000000
H	-4.802406000000	-0.549703000000	1.868594000000
H	-3.494170000000	0.026245000000	0.901941000000
C	-5.338421000000	-0.115808000000	-0.111350000000
H	-4.814343000000	-0.243740000000	-1.063787000000
H	-6.191177000000	-0.801287000000	-0.110946000000
C	-5.779545000000	1.321475000000	0.077909000000
H	-4.893088000000	1.967504000000	0.093208000000
H	-6.258952000000	1.430888000000	1.059309000000
C	-6.732334000000	1.764143000000	-1.018321000000
H	-7.635477000000	1.145805000000	-1.036292000000
H	-6.263165000000	1.691429000000	-2.004413000000
H	-7.044778000000	2.801167000000	-0.876877000000



51A-gR

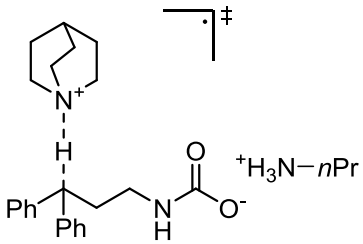
C	-1.451322000000	-0.576503000000	0.050295000000
H	-1.779518000000	-1.367629000000	0.742372000000
H	-1.373670000000	-1.073091000000	-0.931597000000
C	-2.449928000000	0.526976000000	0.018637000000
N	-6.057884000000	0.952506000000	-0.067506000000
C	-4.830090000000	1.409944000000	-0.033018000000
O	-5.940472000000	-0.450799000000	-0.095555000000
C	-4.630417000000	-0.794980000000	-0.078344000000
C	-3.847985000000	0.355230000000	-0.031025000000
C	-4.571007000000	2.869541000000	0.001838000000
H	-5.508308000000	3.427625000000	0.001087000000
H	-4.001872000000	3.144418000000	0.895530000000
H	-3.978808000000	3.182142000000	-0.864061000000
C	-4.344565000000	-2.244447000000	-0.096403000000
H	-4.192036000000	-2.642765000000	0.913696000000
H	-5.180270000000	-2.788842000000	-0.541187000000
H	-3.443567000000	-2.462579000000	-0.673375000000
H	-2.075081000000	1.550790000000	0.006806000000
H	0.742447000000	-1.903149000000	1.175879000000
N	0.893860000000	-1.168707000000	0.500874000000
C	-0.064520000000	-0.091489000000	0.452452000000
C	2.210463000000	-1.046292000000	0.087041000000
H	-0.132516000000	0.436261000000	1.418515000000
H	0.311405000000	0.632404000000	-0.275413000000
O	2.528595000000	-0.018492000000	-0.596532000000
O	2.988782000000	-2.002748000000	0.409779000000
H	4.493958000000	-1.601436000000	-0.270393000000
N	5.006426000000	-0.811389000000	-0.751802000000
H	5.482483000000	-1.121291000000	-1.594455000000
H	4.129425000000	-0.251015000000	-0.970792000000
C	5.894030000000	-0.073359000000	0.172987000000
H	5.296119000000	0.135018000000	1.065958000000
H	6.711559000000	-0.736202000000	0.472328000000
C	6.416276000000	1.208161000000	-0.444384000000
H	5.565617000000	1.830446000000	-0.748649000000
H	6.970577000000	0.971831000000	-1.362067000000

C	7.307370000000	1.972270000000	0.518660000000
H	8.175045000000	1.375958000000	0.818727000000
H	6.764586000000	2.245949000000	1.428823000000
H	7.680537000000	2.894289000000	0.067341000000



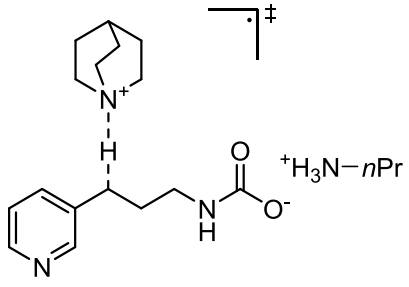
52A-gR

C	-0.920695000000	-0.162381000000	-0.461076000000
H	-1.379310000000	-1.092779000000	-0.811498000000
H	-0.147756000000	0.134019000000	-1.180407000000
C	-1.947918000000	0.899901000000	-0.346417000000
H	-1.626275000000	1.939217000000	-0.315424000000
H	0.583480000000	-2.386842000000	0.786262000000
N	0.845189000000	-1.412772000000	0.789320000000
C	-0.207774000000	-0.431694000000	0.881228000000
C	2.047499000000	-1.138449000000	0.156684000000
H	-0.940571000000	-0.774549000000	1.619623000000
H	0.225897000000	0.501015000000	1.253974000000
O	2.302983000000	0.084187000000	-0.103673000000
O	2.805530000000	-2.132953000000	-0.083159000000
H	4.208672000000	-1.466107000000	-0.782470000000
N	4.668570000000	-0.540611000000	-1.004314000000
H	4.950179000000	-0.484092000000	-1.979066000000
H	3.800352000000	0.043289000000	-0.807730000000
C	5.765056000000	-0.208423000000	-0.068737000000
H	5.370107000000	-0.380500000000	0.937503000000
H	6.582784000000	-0.918002000000	-0.226337000000
C	6.233058000000	1.223612000000	-0.233096000000
H	5.379669000000	1.897015000000	-0.086401000000
H	6.575627000000	1.379310000000	-1.264483000000
C	7.345567000000	1.567085000000	0.741402000000
H	8.215880000000	0.918542000000	0.598327000000
H	7.014742000000	1.451416000000	1.778303000000
H	7.678866000000	2.599553000000	0.614488000000
C	-5.203089000000	-0.520982000000	-0.006838000000
N	-3.861531000000	-0.588988000000	-0.166806000000
C	-5.731483000000	0.755545000000	0.098469000000
C	-6.008037000000	-1.774125000000	0.045436000000
C	-3.302733000000	0.630739000000	-0.190373000000
S	-4.496187000000	1.942421000000	-0.004310000000
H	-6.770266000000	1.030289000000	0.226670000000
H	-7.071394000000	-1.561729000000	0.171110000000
H	-5.878423000000	-2.356772000000	-0.871378000000
H	-5.683666000000	-2.409283000000	0.875062000000



TS_HAT_45A_gH

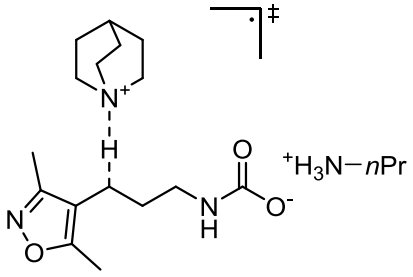
C	-0.015952000000	0.525226000000	-1.105876000000
H	0.474397000000	0.412800000000	-2.079992000000
H	-0.538366000000	-0.414774000000	-0.896799000000
C	0.996501000000	0.814788000000	-0.014619000000
H	1.666247000000	-0.250497000000	-0.038234000000
C	0.394054000000	0.809999000000	1.351001000000
C	0.412246000000	1.931790000000	2.199231000000
C	-0.292972000000	-0.338191000000	1.788668000000
C	-0.228567000000	1.901220000000	3.433217000000
C	-0.921919000000	-0.373629000000	3.024979000000
C	-0.890784000000	0.748706000000	3.855239000000
H	0.901759000000	2.844461000000	1.870269000000
H	-0.342653000000	-1.210734000000	1.139053000000
H	-0.220355000000	2.785569000000	4.063297000000
H	-1.442615000000	-1.272551000000	3.341742000000
H	-1.387503000000	0.727313000000	4.820753000000
C	2.059563000000	1.810270000000	-0.301998000000
C	3.072295000000	2.044884000000	0.652850000000
C	2.178592000000	2.448425000000	-1.551108000000
C	4.141539000000	2.886482000000	0.378976000000
C	3.245314000000	3.298047000000	-1.822285000000
C	4.233166000000	3.519246000000	-0.862297000000
H	3.017362000000	1.546775000000	1.618782000000
H	1.424973000000	2.291578000000	-2.317226000000
H	4.908842000000	3.046067000000	1.130573000000
H	3.306480000000	3.790322000000	-2.788433000000
H	5.069083000000	4.177023000000	-1.080453000000
N	2.505763000000	-1.443044000000	-0.093391000000
C	2.592823000000	-3.858752000000	-0.539928000000
C	1.751138000000	-2.572018000000	-0.678741000000
H	1.548861000000	-2.320284000000	-1.724045000000
H	0.790664000000	-2.647645000000	-0.159441000000
C	4.053478000000	-2.846408000000	1.200693000000
C	2.946536000000	-1.773171000000	1.277669000000
H	3.290582000000	-0.850009000000	1.754994000000
H	2.065499000000	-2.122001000000	1.825203000000
C	4.483525000000	-2.387894000000	-1.207591000000
C	3.667478000000	-1.104135000000	-0.943672000000
H	4.249084000000	-0.346796000000	-0.408494000000
H	3.292420000000	-0.645947000000	-1.864461000000
C	4.031523000000	-3.453789000000	-0.205510000000
H	2.551199000000	-4.431374000000	-1.470727000000
H	2.187900000000	-4.498736000000	0.251201000000
H	4.691383000000	-4.324211000000	-0.253132000000
H	5.033699000000	-2.403097000000	1.405202000000
H	3.880942000000	-3.611959000000	1.962308000000
H	5.551286000000	-2.176111000000	-1.102701000000
H	4.323715000000	-2.741103000000	-2.231784000000
N	-2.122954000000	1.309404000000	-2.149959000000
H	-2.021522000000	1.630993000000	-3.100820000000
C	-1.116959000000	1.614623000000	-1.185088000000
C	-3.098668000000	0.331260000000	-1.935864000000
H	-0.669094000000	2.585932000000	-1.422944000000
H	-1.583421000000	1.687251000000	-0.196766000000
O	-3.111424000000	-0.205404000000	-0.779907000000
O	-3.877292000000	0.093285000000	-2.899903000000
N	-5.420542000000	-1.365686000000	-1.258634000000
H	-5.204743000000	-1.042736000000	-2.221602000000
H	-5.601879000000	-2.365948000000	-1.239066000000
H	-4.484729000000	-1.120899000000	-0.813043000000
C	-6.513801000000	-0.573245000000	-0.640644000000
H	-6.263538000000	0.477234000000	-0.816652000000
H	-7.441262000000	-0.787902000000	-1.178747000000
C	-6.642928000000	-0.864731000000	0.840361000000
H	-5.681866000000	-0.660607000000	1.329032000000
H	-6.845355000000	-1.933532000000	0.986826000000
C	-7.742778000000	-0.035276000000	1.479008000000
H	-8.715508000000	-0.240749000000	1.021466000000
H	-7.546136000000	1.035791000000	1.370797000000
H	-7.828629000000	-0.249033000000	2.546406000000



TS_HAT_49A_gH

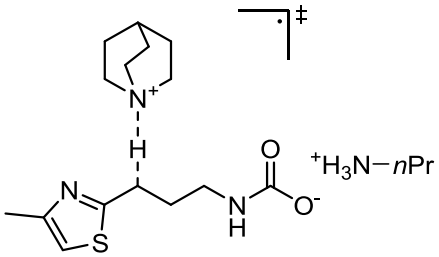
C	-0.021804000000	0.285294000000	-0.527602000000
H	0.380938000000	0.270123000000	-1.548706000000
H	-0.429531000000	-0.710183000000	-0.325078000000
C	1.027786000000	0.639037000000	0.478280000000
H	1.935248000000	-0.291823000000	0.351058000000
C	1.792443000000	1.873145000000	0.335415000000
C	2.439532000000	2.432270000000	1.460421000000

C	1.991301000000	2.528721000000	-0.895419000000
N	3.216524000000	3.510852000000	1.430568000000
C	2.788148000000	3.661263000000	-0.938236000000
C	3.386018000000	4.109967000000	0.242138000000
H	2.299260000000	1.965307000000	2.437205000000
H	1.523182000000	2.152396000000	-1.802658000000
H	2.953715000000	4.193519000000	-1.869512000000
H	4.028055000000	4.987873000000	0.236736000000
N	2.954870000000	-1.196524000000	0.226085000000
C	3.566164000000	-3.538457000000	-0.190494000000
C	2.429675000000	-2.496300000000	-0.251211000000
H	2.060394000000	-2.338330000000	-1.268898000000
H	1.577580000000	-2.767571000000	0.378036000000
C	4.917106000000	-2.142557000000	1.364455000000
C	3.606234000000	-1.350435000000	1.548109000000
H	3.776249000000	-0.349954000000	1.957225000000
H	2.893630000000	-1.865358000000	2.198565000000
C	4.977242000000	-1.691537000000	-1.080749000000
C	3.908728000000	-0.628039000000	-0.754823000000
H	4.339478000000	0.270917000000	-0.301446000000
H	3.340844000000	-0.321111000000	-1.638401000000
C	4.894217000000	-2.794499000000	-0.021381000000
H	3.565550000000	-4.139226000000	-1.104029000000
H	3.409647000000	-4.225437000000	0.647559000000
H	5.732954000000	-3.487227000000	-0.128328000000
H	5.782211000000	-1.477830000000	1.454690000000
H	5.006216000000	-2.896045000000	2.151730000000
H	5.968068000000	-1.229297000000	-1.089905000000
H	4.807410000000	-2.111301000000	-2.077462000000
N	-2.256372000000	0.950412000000	-1.387771000000
H	-2.142397000000	1.130332000000	-2.374827000000
C	-1.210968000000	1.296704000000	-0.487946000000
C	-3.296871000000	0.073002000000	-1.048828000000
H	-0.828550000000	2.296939000000	-0.724246000000
H	-1.623801000000	1.310011000000	0.523449000000
O	-3.365231000000	-0.314739000000	0.148493000000
O	-4.081404000000	-0.218111000000	-2.006652000000
N	-5.801558000000	-1.377292000000	-0.405862000000
H	-5.286432000000	-1.047057000000	-1.280647000000
H	-6.084594000000	-2.351605000000	-0.477165000000
H	-5.022965000000	-1.276026000000	0.269639000000
C	-6.934816000000	-0.480055000000	-0.066048000000
H	-6.532104000000	0.537320000000	-0.078402000000
H	-7.666855000000	-0.553547000000	-0.874762000000
C	-7.551876000000	-0.814548000000	1.276106000000
H	-6.781671000000	-0.747971000000	2.054374000000
H	-7.896947000000	-1.856354000000	1.269561000000
C	-8.708585000000	0.113498000000	1.603551000000
H	-9.501473000000	0.041554000000	0.852752000000
H	-8.382794000000	1.157450000000	1.641514000000
H	-9.148046000000	-0.130821000000	2.572822000000
H	0.728305000000	0.452162000000	1.517270000000
C	3.674436000000	-1.234911000000	1.196235000000
H	4.019888000000	-0.196167000000	1.223523000000
H	3.119150000000	-1.433071000000	2.118459000000
C	4.268950000000	-2.521335000000	-1.428377000000
C	3.416863000000	-1.252120000000	-1.221787000000
H	4.026344000000	-0.343987000000	-1.179798000000
H	2.664857000000	-1.122269000000	-2.005607000000
C	4.385596000000	-3.245073000000	-0.083943000000
H	2.719089000000	-4.625816000000	-0.340327000000
H	3.024540000000	-4.163982000000	1.330722000000
H	5.109192000000	-4.061032000000	-0.154557000000
H	5.730662000000	-1.710918000000	0.650327000000
H	5.067208000000	-2.732388000000	1.920945000000
H	5.254420000000	-2.246301000000	-1.814050000000
H	3.803388000000	-3.177319000000	-2.171161000000
N	-2.293891000000	1.322069000000	-1.344193000000
H	-2.209495000000	1.657118000000	-2.292720000000
C	-1.213003000000	1.517106000000	-0.435424000000
C	-3.291266000000	0.363681000000	-1.129373000000
H	-0.800450000000	2.525794000000	-0.561147000000
H	-1.600403000000	1.434104000000	0.583363000000
O	-3.292117000000	-0.229336000000	-0.012488000000
O	-4.111126000000	0.208713000000	-2.087727000000
N	-5.676636000000	-1.306804000000	-0.627720000000
H	-5.273713000000	-0.805528000000	-1.474155000000
H	-5.904360000000	-2.275951000000	-0.834397000000
H	-4.830770000000	-1.245117000000	-0.023677000000
C	-6.817291000000	-0.568046000000	-0.030770000000
H	-6.489380000000	0.471258000000	0.067323000000
H	-7.640493000000	-0.586806000000	-0.750149000000
C	-7.231799000000	-1.143739000000	1.307663000000
H	-6.371172000000	-1.127184000000	1.988045000000
H	-7.507446000000	-2.198721000000	1.182132000000
C	-8.391328000000	-0.372020000000	1.912521000000
H	-9.269555000000	-0.395072000000	1.259974000000
H	-8.128371000000	0.677620000000	2.076028000000
H	-8.685206000000	-0.792882000000	2.876325000000
H	0.697717000000	0.439700000000	1.423817000000
N	3.172599000000	3.559090000000	1.109655000000
C	2.477891000000	2.508592000000	1.475095000000
O	3.001953000000	3.654605000000	-0.290526000000
C	1.825557000000	1.878815000000	0.359843000000
C	2.402092000000	2.122853000000	2.905438000000
C	2.208887000000	2.665660000000	-0.719941000000
H	2.983571000000	2.812344000000	3.517873000000
H	1.365468000000	2.137198000000	3.255286000000
H	2.784012000000	1.110774000000	3.070220000000
C	1.921727000000	2.644870000000	-2.168371000000
H	2.202607000000	1.688985000000	-2.620259000000
H	0.854308000000	2.792773000000	-2.362256000000
H	2.471894000000	3.439758000000	-2.672204000000



TS_HAT_51A_gH

C	-0.073300000000	0.473527000000	-0.613790000000
H	0.307740000000	0.540957000000	-1.639772000000
H	-0.519809000000	-0.519610000000	-0.497298000000
C	1.013532000000	0.683115000000	0.400668000000
H	1.841664000000	-0.326754000000	0.201847000000
N	2.709623000000	-1.358994000000	0.077085000000
C	3.006359000000	-3.788992000000	0.302181000000
C	1.979489000000	-2.647842000000	0.161781000000
H	1.381604000000	-2.736169000000	-0.749814000000
H	1.292156000000	-2.590496000000	1.010787000000
C	4.826211000000	-2.233178000000	0.978433000000



TS_HAT_52A_gH

C	-0.129327000000	0.460345000000	-0.440947000000
H	0.301800000000	0.538128000000	-1.445131000000
H	-0.662208000000	-0.493103000000	-0.365012000000
C	0.945582000000	0.544054000000	0.603177000000
H	1.688059000000	-0.494260000000	0.382357000000
N	2.498767000000	-1.594597000000	0.141705000000
C	2.565649000000	-3.978084000000	-0.455221000000
C	1.688156000000	-2.711508000000	-0.396385000000
H	1.334285000000	-2.403328000000	-1.384849000000
H	0.814613000000	-2.835637000000	0.249821000000
C	4.240634000000	-3.028271000000	1.121756000000
C	3.141312000000	-1.988151000000	1.416927000000
H	3.536868000000	-1.082485000000	1.887345000000
H	2.353424000000	-2.386065000000	2.063142000000
C	4.320676000000	-2.422978000000	-1.288870000000
C	3.524752000000	-1.178658000000	-0.844649000000
H	4.158193000000	-0.433262000000	-0.352529000000
H	3.012502000000	-0.686622000000	-1.676702000000
C	4.029655000000	-3.555603000000	-0.300114000000
H	2.405823000000	-4.496131000000	-1.404926000000
H	2.287976000000	-4.674781000000	0.342537000000
H	4.691060000000	-4.404687000000	-0.491207000000
H	5.232772000000	-2.574115000000	1.211339000000
H	4.190238000000	-3.838814000000	1.854112000000
H	5.388706000000	-2.190075000000	-1.315848000000
H	4.030317000000	-2.722094000000	-2.301382000000
N	-2.250869000000	1.499982000000	-1.198723000000
H	-2.120934000000	1.859477000000	-2.133180000000
C	-1.177843000000	1.594740000000	-0.264335000000
C	-3.307544000000	0.594866000000	-1.043174000000
H	-0.673850000000	2.560038000000	-0.382051000000
H	-1.591651000000	1.534069000000	0.745679000000
O	-3.367370000000	-0.045259000000	0.044015000000
O	-4.113334000000	0.531374000000	-2.025273000000
N	-5.770226000000	-1.014746000000	-0.713320000000
H	-5.304796000000	-0.459039000000	-1.496377000000
H	-6.011895000000	-1.956372000000	-1.012100000000
H	-4.961897000000	-1.033751000000	-0.061446000000
C	-6.924261000000	-0.293037000000	-0.122198000000
H	-6.568248000000	0.715993000000	0.106777000000
H	-7.691699000000	-0.202869000000	-0.895875000000
C	-7.458542000000	-0.984218000000	1.115292000000
H	-6.652495000000	-1.075130000000	1.854092000000
H	-7.760992000000	-2.007866000000	0.859508000000
C	-8.633067000000	-0.229831000000	1.713108000000
H	-9.459406000000	-0.148700000000	1.000139000000
H	-8.347086000000	0.785535000000	2.004189000000
H	-9.013653000000	-0.734041000000	2.603843000000
H	0.608218000000	0.331056000000	1.623732000000
N	2.179006000000	2.304912000000	-0.574244000000
C	3.133097000000	3.246316000000	-0.350282000000
C	3.585268000000	3.315039000000	0.960505000000
C	3.605330000000	4.109809000000	-1.463530000000
C	1.863949000000	1.653095000000	0.532354000000
S	2.779122000000	2.179843000000	1.947212000000
H	4.328550000000	3.988474000000	1.366526000000
H	4.400909000000	4.782341000000	-1.140635000000
H	3.976648000000	3.501756000000	-2.293234000000
H	2.781913000000	4.713536000000	-1.856382000000

10. References

1. M. S. Lowry, J. L. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, Single-layer electroluminescent devices and photoinduced hydrogen production from an ionic iridium(III) complex. *Chem. Mater.* **17**, 5712–5719 (2005).
2. S. Ladouceur, D. Fortin, E. Zysman-Colman, Enhanced luminescent Iridium(III) complexes bearing aryltriazole cyclometallated ligands. *Inorg. Chem.* **50**, 11514–11526 (2011).
3. J. C. Chu, T. Rovis, Amide-directed photoredox-catalysed C–C bond formation at unactivated sp^3 C–H bonds. *Nature* **539**, 272–275 (2016).
4. K. Masuda, Y. Ito, M. Horiguchi, H. Fujita, Studies on the solvent dependence of the carbamic acid formation from ω-(1-naphthyl)alkylamines and carbon dioxide. *Tetrahedron* **61**, 213–229 (2005).
5. N. Armanino, E. M. Carreira, Ruthenium-catalyzed intramolecular hydrocarbamoylation of allylic formamides: convenient access to chiral pyrrolidones. *J. Am. Chem. Soc.* **135**, 6814−6817 (2013).
6. A. L. Smith, S. F. Williams, A. B. Holmes, L. R. Hughes, C. Swithenbank, Z. Lidert, Stereoselective synthesis of (±)-Indolizidines 167B, 205A, and 207A. Enantioselective synthesis of (–)-Indolizidine 209B. *J. Am. Chem. Soc.* **110**, 8696-8698 (1988).
7. Das, S., Kumar, J. S. D., Thomas, K. G., Shivaramayya, K. & George, M. V. Photocatalyzed multiple additions of amines to α,β-unsaturated esters and nitriles. *J. Org. Chem.* **59**, 628–634 (1994).
8. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc.,

Wallingford CT, 2013.

9. C. J. Cramer, Essentials of Computational Chemistry: Theories and Models; 2nd ed.; Wiley: New York, USA, 2004.
10. R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, Use of solution-phase vibrational frequencies in continuum models for the free energy of solvation. *J. Phys. Chem. B* **115**, 14556–14562 (2011).
11. Funes-Ardoiz, I.; Paton, R. S. (2016). GoodVibes: GoodVibes v1.0.2. http://doi.org/10.5281/zenodo.595246 (accessed November 3, 2017).
12. C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **139**, 134101 (2013).
13. DLPNO-CCSD(T) has been shown to be able to recover ~99.9% of total correlation energy of full CCSD(T), see: M. Saitow, U. Becker, C. Riplinger, E. F. Valeev, F. Neese, A new near-linear scaling, efficient and accurate, open-shell domain-based local pair natural orbital coupled cluster singles and doubles theory. *J. Chem. Phys.* **146**, 164105 (2017); it has also been shown to yield high accuracy results in a diverse set of applications, see: D. G. Liakos, M. Sparta, M. K. Kesharwani, J. M. L. Martin, F. Neese, Exploring the accuracy limits of local pair natural orbital coupled-cluster theory. *J. Chem. Theory Comput.* **11**, 1525–1539 (2015).
14. F. Neese, The ORCA program system. *WIREs Comput. Mol. Sci.* **2**, 73–78 (2012).
15. F. Neese, Software update: the ORCA program system, version 4.0. *WIREs Comput. Mol. Sci.* doi: 10.1002/wcms.1327 (2017).
16. S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456–1465 (2011).